(FILE 'HOME' ENTERED AT 15:21:02 ON 10 APR 2002)

FILE 'CAPLUS, USPATFULL' ENTERED AT 15:21:19 ON 10 APR 2002

L1	48325	S	HYDROGENATION CATALYST
L2	0	S	L1 AND PDCACO3
L3	4	S	L1 AND PDPT?
L4	4	S	L1 AND PDNI?
L5	2380	S	L1 AND 1,4-BUTENEDIOL OR BUTENE-1,4-DIOL
L6	45	S	L5 AND 1,4-BUTYNEDIOL OR 1,4-BUTINEDIOL
L7	10	S	L6 AND PLATINUM
L8	5	S	L7 AND PALLADIUM
L9	5	S	L8 AND NICKEL
L10	24	S	1,4-BUTYNEDIOL (P) 1,4-BUTENEDIOL (P) HYDROGENAT?
L11	9	S	L10 AND PLATINUM
L12	5	S	L11 AND PALLADIUM
L13	5	S	L12 AND NICKEL
L14	2188	S	HYDROGENATION CATALYST/TI
L15	13	S	1,4-BUTENEDIOL/TI
L16	0	S	L14 AND L15
L17	461	S	1,4-BUTYNEDIOL
L18	6	S	L14 AND L17
L19	4	S	HYDROGENATION OF 1,4-BUTYNEDIOL TO 1,4-BUTENEDIOL

L14 ANSWER 1 OF 11 CAPLUS COPYRIGHT 2002 ACS
AN 1972:461316 CAPLUS
DN 77:61316
TI Synthesis of 2-acetyl-2-cyclohexen-1-one
AU Akhrem, A. A.; Moiseenko, A. M.; Lakhvich, F. A.
CS Inst. Org. Khim. im. Zelinskogo, Moscow, USSR
SO Izv. Akad. Nauk SSSR, Ser. Khim. (1972), (2), 407-15
CODEN: IASKA6
DT Journal
LA Russian

L14 ANSWER 2 OF 11 CAPLUS COPYRIGHT 2002 ACS
AN 1967:400786 CAPLUS
DN 67:786
TI Gibberellin in immature seeds of Pharbitis nil
AU Takahashi, Nobutaka; Murofushi, Noboru; Yokota, Takao; Tamura, Saburo
CS Univ. Tokyo, Tokyo, Japan
SO Tetrahedron (1967), (12), 1065-8
CODEN: TETRAB
DT Journal
LA English

L14 ANSWER 3 OF 11 CAPLUS COPYRIGHT 2002 ACS
AN 1966:52244 CAPLUS
DN 64:52244
OREF 64:9780e-h,9781a-b
TI Synthesis in the series of Lycopodium alkaloids. III. Novel system active in photochemical additions
AU Boehme, E.H. W.; Valenta, Z.; Wiesner, K.
CS Univ. New Brunswick, Frederricton, Can.
SO Tetrahedron Letters (1965), (29), 2441-4
DT Journal
LA English

L14 ANSWER 4 OF 11 CAPLUS COPYRIGHT 2002 ACS
AN 1965:58595 CAPLUS
DN 62:58595
OREF 62:10350h,10351a-c
TI Bitter principles of Simarubaceae. XIV. Constituents of Ailanthus altissima seeds. Structure of ailanthone
AU Polonsky, Judith; Fourrey, Jean-Louis
CS C.N.R.S., Gif-sur-Yvette, Fr.
SO Tetrahedron Letters (1964), (52), 3983-90
DT Journal
LA French

L14 ANSWER 5 OF 11 CAPLUS COPYRIGHT 2002 ACS
AN 1959:23179 CAPLUS
DN 53:23179
OREF 53:4229b-i,4230a-h
TI Reactions with microorganisms. IV. Stereospecific reduction of .+-.-9-methyl-cis-1,6-decahydronaphthalenedione with Rhizopus nigricans. Direct configurative correlation of microbiologically produced 9-methyldecahydronaphthalene derivatives with steroids
AU Acklin, W.; Prelog, V.; Zach, D.
CS Eidgenoss. Tech. Hochschule, Zurich, Switz.
SO Helv. Chim. Acta (1958), 41, 1428-37
DT Journal
LA Unavailable

L14 ANSWER 6 OF 11 CAPLUS COPYRIGHT 2002 ACS
AN 1958:113940 CAPLUS
DN 52:113940
OREF 52:20252f-i,20253a-i,20254a-e
TI Modified steroid hormones. IX. 2- and 4-Chloro derivatives of 17.gamma.-propionoxyandrosta-1,4-dien-3-one and -1,4,6-trien-3-one
AU Kirk, David N.; Petrow, Vladimir
CS Brit. Drug Houses Ltd., London
SO J. Chem. Soc. (1958) 1334-42
DT Journal
LA Unavailable

L14 ANSWER 7 OF 11 CAPLUS COPYRIGHT 2002 ACS
AN 1958:113107 CAPLUS
DN 52:113107
OREF 52:19925i,19926a-b
TI Partial hydrogenation of 1,4-butynediol. II. The role of calcium carbonate as a carrier of the palladium catalyst
AU Fukuda, Tosao
CS Yokohama Natl. Univ.
SO Bull. Chem. Soc. Japan (1958), 31, 343-7
DT Journal
LA Unavailable

L14 ANSWER 8 OF 11 CAPLUS COPYRIGHT 2002 ACS
AN 1957:29686 CAPLUS
DN 51:29686
OREF 51:5696a-f
TI (+)-.beta.-Aminobutyric acid. Correlation of its configuration with that of .alpha.-amino acids
AU Balenovic, K.; Bregant, N.; Cerar, D.
CS Kemijski Inst., Zagreb, Yugoslav.
SO J. Chem. Soc. (1956) 3982-4
DT Journal
LA Unavailable

L14 ANSWER 9 OF 11 CAPLUS COPYRIGHT 2002 ACS
AN 1953:12204 CAPLUS
DN 47:12204
OREF 47:2184i,2185a-c
TI Erythrina alkaloids. III. The Hofmann degradation of tetrahydroerysotrine and tetrahydroerythraline
AU Kenner, G. W.; Khorana, H. G.; Prelog, V.
CS Eidg. Tech. Hochschule, Zurich, Switz.
SO Helv. Chim. Acta (1951), 34, 1969-74
DT Journal
LA German

L14 ANSWER 10 OF 11 CAPLUS COPYRIGHT 2002 ACS
AN 1953:9244 CAPLUS
DN 47:9244
OREF 47:1674d-i,1675a-i,1676a-i,1677a-b
TI The oxidation of phenols. XI. Dehydrotetrachloro-p-cresol, a radical with monovalent oxygen
AU Pummerer, Rudolf; Schmidutz, Georg; Seifert, Helmut
CS Univ. Erlangen, Germany
SO Chem. Ber. (1952), 85, 535-55
DT Journal

LA Unavailable

L14 ANSWER 11 OF 11 CAPLUS COPYRIGHT 2002 ACS
AN 1949:8309 CAPLUS
DN 43:8309
OREF 43:1751h-i,1752a-h
TI Diterpenes. LVII. The constitution of agathenedioic acid
AU Ruzicka, L.; Zwicky, R.; Jeger, O.
SO Helv. Chim. Acta (1948), 31, 2143-7
DT Journal
LA German

=> d l14 kwic tot

L14 ANSWER 1 OF 11 CAPLUS COPYRIGHT 2002 ACS
AB . . . and some 2-cyclohexenone analog (IV) of III. Heating V with Pd black in cyclohexene gave o-HOC6H4Ac. Hydrogenation of III over **PdBaCO3** gave VI. IV and KCN in DMF at room temp. gave 2-acetyl-5,5-dimethyl-3-cyanocyclohexanone. Thus, the cross-conjugated diketone, IV, tends to isomerize. . .

L14 ANSWER 2 OF 11 CAPLUS COPYRIGHT 2002 ACS
AB . . . to PG. The assignment was confirmed by catalytic hydrogenation of GA5 Me ester (II) in the presence of partially poisoned **PdBaCO3** and sepn. of the products over silica gel impregnated with AgNO3 to give I
(R = Me) and III in. . .

L14 ANSWER 3 OF 11 CAPLUS COPYRIGHT 2002 ACS
AB . . . sepd. by preparative vapor phase chromatography gave equal amts. of VIII, m. 85.degree.; and IX, m. 118.degree.. IX hydrogenated over **PdBaCO3** in alc. gave a mixt. of products (X, XI). IX converted to a ketal with HOCH2CH2OH, hydrogenated over prereduced PtO2,. . .

L14 ANSWER 4 OF 11 CAPLUS COPYRIGHT 2002 ACS
AB . . . 30.5.degree. (CHCl3). The N.M.R. spectrum of VI was distinctly analogous to that of V triacetate. Selective hydrogenation of VI over **PdBaCO3** gave dihydroailanthone triacetate, m. 269-72.degree., [.alpha.]D 64.degree. (CHCl3). Methoxychaparrinone was oxidized to give VII, identical with a product obtained previously. . .

L14 ANSWER 5 OF 11 CAPLUS COPYRIGHT 2002 ACS
AB . . . (IV). Racemic 3,4,8,8a-tetrahydro-8a-methyl-1,6(2H, 7H)-naphthalenedione (1.25 g., m. 52.degree.) in 50 ml. abs. alc. hydrogenated 50 min. with 600 mg. 5% **PdBaCO3** and the filtered soln. evapd. gave 691 mg. I-II mixt., m. 67-8.degree. (Et2O-petr. ether). Evapn. of the mother liquors yielded. . .

L14 ANSWER 6 OF 11 CAPLUS COPYRIGHT 2002 ACS
AB . . . heated 4 hrs. on the steam bath gave V. V (250 mg.) in 200 ml. MeOH reduced over 20 mg. **PdBaCO3** until 1 mole H had been absorbed, then chromatographed gave 60 mg. XII, .lambda. 256 m.mu., log .epsilon. 4.15. III. . .

L14 ANSWER 7 OF 11 CAPLUS COPYRIGHT 2002 ACS
AB . . . are given. Catalyst carriers studied were CaCO3, BaCO3, Al2O3, BaSO4, and C. Partial hydrogenation of III can be achieved with **PdBaCO3** poisoned by both I and II. CaCO3 as carrier seems to suppress polymerization accompanying hydrogenation, but does not increase

catalytic. . .

L14 ANSWER 8 OF 11 CAPLUS COPYRIGHT 2002 ACS
AB . . . chloride (X), m. 92.degree. (from C6H6-ligroine), [.alpha.]20D 65.degree. (c 0.43, C6H6). X (4.6 g.) in 20 cc. xylene reduced with **PdBaCO3** at 110-15.degree. so that 0.7 mole H was taken up during 5 hrs. gave 1.8 g. III, sublimed at 110.degree./0.016. . .

L14 ANSWER 9 OF 11 CAPLUS COPYRIGHT 2002 ACS
AB . . . oil, [.alpha.]D20 -70.degree. after redistn. in a high vacuum. III (30.4 mg.) absorbed 1 mole H with 100 mg. 2% **PdBaCO3** to give de-N-methylhexahydroerysotrine, [.alpha.]D20 17.degree.. Similarly the methohydroxide from 529 mg. II gave 319 mg. de-N-Me deriv. of II as. .
.

L14 ANSWER 10 OF 11 CAPLUS COPYRIGHT 2002 ACS
AB . . . with 4 g. AlBr3 in 40 cc. C6H6 4 hrs. gives 93% V. Refluxing
200
mg. XXII with 6 g. **PdBaCO3** and 6 g. N2H4.H2O in 200 cc. EtOH and 10 cc. 10% alc. KOH 3 hrs. with stirring give 96%. . .

L14 ANSWER 11 OF 11 CAPLUS COPYRIGHT 2002 ACS
AB . . . drops C5H5N at 0.degree. 4 hrs., b0.02 140-3.degree.. Reduction of 400 mg. VI according to Rosenmund in the presence of **PdBaCO3** catalyst 6 hrs. and chromatographic fractionation of the neutral products (350 mg.) give 12 fractions. Fractions 3-6, 110 mg., eluted. . .

=>

L33 ANSWER 1 OF 4 CAPLUS COPYRIGHT 2002 ACS
AN 1987:557919 CAPLUS
DN 107:157919
TI Kinetics and FTIR studies of hydrocarbon synthesis on palladium/ZSM5 catalysts
AU Thomson, R.; Wolf, E. E.
CS Dep. Chem. Eng., Univ. Notre Dame, Notre Dame, IN, USA
SO Report (1986), DOE/PC/70788-T5; Order No. DE87001708, 55 pp. Avail.: NTIS
From: Energy Res. Abstr. 1987, 12(6), Abstr. No. 10720
DT Report
LA English
AB Hydrocarbon synthesis during CO **hydrogenation** over Pd/M-ZSM5 (M = H, Na, La) and Pd/SiO2 was investigated. Overall activity depended on the cation-exchanged form of the support and decreased in the order Pd/La-ZSM5 = Pd/Na-ZSM5 > Pd/H-ZSM5 > Pd/SiO2. The zeolite-supported catalysts showed high selectivity towards satd. C2-6 hydrocarbons, whereas Pd/SiO2 favored MeOH prodn. Increasing temp. and H/CO feed ratio led to higher reaction rates, lower yields of C2-6 products, and increased lighter hydrocarbons. A mech. mixt. of Pd/SiO2 and Na-ZSM5 showed similar product distribution as Pd/Na-ZSM5. IR spectra of the catalysts under reaction conditions indicated the presence of adsorbed oxygenates on the zeolite. Change in the IR bands during the initial stages of the reaction indicated that surface species on the zeolite were not MeOH synthesis intermediates. The effects of various temps. and H/CO ratios on the spectra were small. The kinetic and IR results indicated that C2+ hydrocarbon synthesis over **Pd/ZSM5** followed a biffunctional reaction pathway, involving MeOH synthesis and conversion of MeOH to hydrocarbons on the zeolite support.

L33 ANSWER 1 OF 4 CAPLUS COPYRIGHT 2002 ACS

AB Hydrocarbon synthesis during CO **hydrogenation** over Pd/M-ZSM5 (M = H, Na, La) and Pd/SiO2 was investigated. Overall activity depended on the cation-exchanged form of the. . . temps. and H/CO ratios on the spectra were small. The kinetic and IR results indicated that C2+ hydrocarbon synthesis over **Pd/ZSM5** followed a biffunctional reaction pathway, involving MeOH synthesis and conversion of MeOH to hydrocarbons on the zeolite support.

ST carbon monoxide **hydrogenation** hydrocarbon synthesis; methanol synthesis carbon monoxide **hydrogenation**; FTIR hydrocarbon synthesis catalysis kinetics

IT **Hydrogenation** catalysts
(palladium/ZSM5, in carbon monoxide to hydrocarbons)

IT Zeolites, uses and miscellaneous
RL: CAT (Catalyst use); USES (Uses)
(HZSM 5, catalysts, in carbon monoxide **hydrogenation** to hydrocarbons)

IT Zeolites, uses and miscellaneous
RL: USES (Uses)
(ZSM 5, lanthanum- and sodium-exchanged, catalysts, in carbon monoxide **hydrogenation** to hydrocarbons)

IT 630-08-0, Carbon monoxide, reactions
RL: RCT (Reactant); RACT (Reactant or reagent)
(**hydrogenation** of, to hydrocarbons, on palladium/ZSM5 catalysts, kinetics and FTIR studies of)

IT 67-56-1P, Methanol, preparation
RL: RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent)
(synthesis of, in carbon monoxide **hydrogenation**, on palladium/ZSM5 catalysts, kinetics and FTIR studies of)

IT 1335-30-4
RL: USES (Uses)
(zeolites, HZSM 5, catalysts, in carbon monoxide **hydrogenation** to hydrocarbons)

IT 1335-30-4
RL: USES (Uses)
(zeolites, ZSM 5, lanthanum- and sodium-exchanged, catalysts, in carbon monoxide **hydrogenation** to hydrocarbons)

```
     (FILE 'HOME' ENTERED AT 14:23:32 ON 20 NOV 2002)

     FILE 'CAPLUS, USPATFULL' ENTERED AT 14:23:42 ON 20 NOV 2002
L1             0 S PD/MGCO3
L2            50 S PALLADIUM (P) MAGNESIUM CARBONATE
L3        337656 S HYDROGENAT?
L4            11 S L2 AND HYDROGENAT?
L5             0 S L4 AND ZSM5-NH4
L6             2 S L4 AND BARIUM CARBONATE
L7             9 S L4 NOT L6

     FILE 'STNGUIDE' ENTERED AT 14:31:07 ON 20 NOV 2002
L8             0 S PDMGCO3
L9             0 S 1,4-BUTYNEDIOL (P) 1,4-BUTENEDIOL (P) PALLADIUM

     FILE 'CAPLUS, USPATFULL' ENTERED AT 14:36:28 ON 20 NOV 2002
L10           10 S 1,4-BUTYNEDIOL (P) 1,4-BUTENEDIOL (P) PALLADIUM
L11            9 S 1,4-BUTYNEDIOL (P) 1,4-BUTENEDIOL (P) PLATINUM
L12            1 S L11 NOT L10
L13            1 S PTCACO3

     FILE 'STNGUIDE' ENTERED AT 14:48:03 ON 20 NOV 2002

     FILE 'CAPLUS, USPATFULL' ENTERED AT 14:50:45 ON 20 NOV 2002
L14           11 S PDBACO3
L15            0 S PDMGCO3
L16            0 S PTMGCO3
L17            0 S PTBACO3
L18            1 S PTCACO3
L19         1685 S LINDLAR? CATALYST
L20          791 S L19 AND PALLADIUM
L21          259 S L20 AND PLATINUM
L22          228 S L21 AND CARBONATE
L23           79 S L22 AND BARIUM
L24           70 S L23 AND MAGNESIUM
L25           60 S L24 AND CALCIUM
L26           53 S L25 AND HYDROGENAT?
L27           30 S L26 AND SUPPORT?
L28            4 S L27 AND ?BUTYNEDIOL
L29           26 S L27 NOT L28
L30           26 DUP REM L29 (0 DUPLICATES REMOVED)

=> d l14 1 2 3 4 7 bib abs

L14  ANSWER 1 OF 11  CAPLUS  COPYRIGHT 2002 ACS
AN   1972:461316  CAPLUS
DN   77:61316
TI   Synthesis of 2-acetyl-2-cyclohexen-1-one
AU   Akhrem, A. A.; Moiseenko, A. M.; Lakhvich, F. A.
CS   Inst. Org. Khim. im. Zelinskogo, Moscow, USSR
SO   Izv. Akad. Nauk SSSR, Ser. Khim. (1972), (2), 407-15
     CODEN: IASKA6
DT   Journal
LA   Russian
GI   For diagram(s), see printed CA Issue.
AB   Pyrolysis in N atm. of I at 120-40.degree. gave AcNH2 and
     2-acetyl-3-cyclohexen-1-one as well as some dimer (II).  Similar
pyrolysis
     of a di-Me analog of I at 180.degree. gave 2-acetyl-5,5-dimethyl-3-
```

cyclohexene-1-one (III) and some 2-cyclohexenone analog (IV) of III. Heating V with Pd black in cyclohexene gave o-HOC6H4Ac. Hydrogenation of III over **PdBaCO3** gave VI. IV and KCN in DMF at room temp. gave 2-acetyl-5,5-dimethyl-3-cyanocyclohexanone. Thus, the cross-conjugated diketone, IV, tends to isomerize to III.

L14 ANSWER 2 OF 11 CAPLUS COPYRIGHT 2002 ACS
AN 1967:400786 CAPLUS
DN 67:786
TI Gibberellin in immature seeds of Pharbitis nil
AU Takahashi, Nobutaka; Murofushi, Noboru; Yokota, Takao; Tamura, Saburo
CS Univ. Tokyo, Tokyo, Japan
SO Tetrahedron (1967), (12), 1065-8
CODEN: TETRAB
DT Journal
LA English
GI For diagram(s), see printed CA Issue.
AB EtOAc-sol. acidic fraction from 60 kg. immature seeds of morning glory (P. nil) was successively subjected to 10 transfers (countercurrent distribution) and chromatographed over charcoal, eluted with 50:50 and 70:30 Me2CO-H2O and the fractions F-I and F-II purified by successive silicic acid adsorption, partition, and preparative thin-layer chromatog. F-I showed a fluorescent spot at RGA3 1.00 on a thin-layer chromatogram and exhibited marked growth promoting activity to dwarf maize mutant d-5. F-I Me ester gave a thin-layer chromatogram fluorescent spot with Rf value identical with that of GA3 Me ester, showing the presence of gibberellin A3 in the seeds. Purified F-II, RGA3 1.60, exhibited growth promoting activity to the 3-5 mutant but weak activity towards rice seedlings. Preparative thin-layer chromatog. gave 7 mg. colorless Me ester, m. 181.degree., RGA3-Me 1.55 (fluorescent), M+ 346 (C20H26O5), v 3520, 1778, 1720, 1670, 882 cm.-1, .tau. 6.33, 4.80, 8.93, showing the presence of OH, lactone, CO2Me, exocyclic methylene, and C-Me groups. Accordingly F-II, C19H24O5, is a new C19 gibberellin, tentatively designated Pharbitis gibberellin (PG). In the high resolution mass spectrum the Me ester gave prominent peaks due to M-32, M-46, M-60, M-78, M-104, M-106, M-122 fragment ions together with C17H17-21 hydrocarbon ion peaks, and suggested the presence of a C-7 OH group, confirmed by comparison of the N.M.R. spectrum with that of C5H5N. The evidence permitted assignment of the structure I to PG. The assignment was confirmed by catalytic hydrogenation of GA5 Me ester (II) in the presence of partially poisoned **PdBaCO3** and sepn. of the products over silica gel impregnated with AgNO3 to give I (R = Me) and III in the ratio of 3:1. I (R = Me) was completely identical with PG Me ester.

L14 ANSWER 3 OF 11 CAPLUS COPYRIGHT 2002 ACS
AN 1966:52244 CAPLUS
DN 64:52244
OREF 64:9780e-h,9781a-b
TI Synthesis in the series of Lycopodium alkaloids. III. Novel system active in photochemical additions
AU Boehme, E.H. W.; Valenta, Z.; Wiesner, K.
CS Univ. New Brunswick, Frederricton, Can.
SO Tetrahedron Letters (1965), (29), 2441-4
DT Journal
LA English
GI For diagram(s), see printed CA Issue.

AB cf. CA 53, 5310g. In efforts to develop methods of potential usefulness in the synthesis of Lycopodium alkaloids attention was turned to annotinine (I), and in this connection it was decided to synthesize the system (II, R = H) (III) and to investigate its behavior in photoaddns. The readily available cyanoethyl deriv. (IV) kept in 20% HCl 4 days gave a quant. yield of III, C9H11NO2, m. 200-1.degree.. III in H2C:CHCO2Et irradiated in a pyrex container 2 days at 0.degree. with a Hg lamp and the product (50% yield) recrystd. gave homogeneous material C14H19NO4, m. 143.degree. reduced with NaBH44 to a mixt. of 2 epimeric alcs. (V), converted by mild alk. hydrolysis followed by acidification to give a 50% yield of the oily lactone-lactam (VI). Photochem. reactions of the N-substituted system were investigated. III in Me2CO refluxed 6 hrs. with an excess of powd. KOH and MeI gave 80% II (R = Me) (VII), C10H13NO2, m. 69.degree.. VII in tetrahydrofuran irradiated at -80.degree. with excess H2C:C:CH2 and the mixt. (50%) sepd. by preparative vapor phase chromatography gave equal amts. of VIII, m. 85.degree.; and IX, m. 118.degree.. IX hydrogenated over **PdBaCO3** in alc. gave a mixt. of products (X, XI). IX converted to a ketal with HOCH2CH2OH, hydrogenated over prereduced PtO2, and deketalized with p-MeC6H4SO3H in MeCO transformed IX stereospecifically to X, m. 112.degree.. When R in II is larger than Me, the allene addn. is completely stereospecific with formation of compds. of type IX. The new photochem. reaction provides a possible route to the synthesis of I, starting with the system XII, and the system XIII may give an exceedingly simple route to lycopodine.

L14 ANSWER 4 OF 11 CAPLUS COPYRIGHT 2002 ACS
AN 1965:58595 CAPLUS
DN 62:58595
OREF 62:10350h,10351a-c
TI Bitter principles of Simarubaceae. XIV. Constituents of Ailanthus altissima seeds. Structure of ailanthone
AU Polonsky, Judith; Fourrey, Jean-Louis
CS C.N.R.S., Gif-sur-Yvette, Fr.
SO Tetrahedron Letters (1964), (52), 3983-90
DT Journal
LA French
GI For diagram(s), see printed CA Issue.
AB cf. Bull. Soc. Chim. France 1964, 2016-19; CA 56, 12843b. In addn. to 2,6-dimethoxybenzoquinone, isolation from A. altissima seeds gave 4 cryst. compds. designated A, B, C, and D (I, II, III, IV). I, m. 238-42.degree., [.alpha.]D -47.degree. (C5H5N) was identical with chaparrinone (V), a bitter principle from Hannoa klaineana. The principal constituent was ailanthone II, m. 234-8.degree., [.alpha.]D 12.5.degree. (alc.). Acetylation of II gave the triacetate (VI), m. 225-8.degree., [.alpha.]D 30.5.degree. (CHCl3). The N.M.R. spectrum of VI was distinctly analogous to that of V triacetate. Selective hydrogenation of VI over **PdBaCO3** gave dihydroailanthone triacetate, m. 269-72.degree., [.alpha.]D 64.degree. (CHCl3). Methoxychaparrinone was oxidized to give VII, identical with a product obtained previously from V. II treated with CHMeN2 gave 11-ethoxyailanthone, m. 258-60.degree., [.alpha.]D -65.degree.(alc.). Similarly, treatment with CH2N2 gave the corresponding 11-methoxyailanthone, m. 255-8.degree., hydrogenated over Pd-BaCO3 to

methoxydihydroailanthone (VIII), m. 244-5.degree., [.alpha.]D -24.degree. (CHCl3). VIII oxidized at 0.degree. by Jones reagent gave VII, m. 234-40.degree., [.alpha.]D -117.degree. (CHCl3). III was difficult to sep. from II by chromatography. The acetyl deriv., m. 160-2.degree., on sapon. yielded III, m. 155-6.degree.. IV, C20H26O7, m. 259-60.degree., gave a diacetate. The name ailantholide was proposed for IV. The biogenetic precursor of the bitter principles of the Simarubaceae should be a tetracyclic triterpene of the type of tirucallol or butyrospermol. The presence of an oxygenated function at C-13 in some constituents and of a vinylidene group in II favors the hypothetical oxidn. at the C-17 level of compds. contg. more than 20 C atoms such as simarolide (CA 62, 1692d).

L14 ANSWER 7 OF 11 CAPLUS COPYRIGHT 2002 ACS
AN 1958:113107 CAPLUS
DN 52:113107
OREF 52:19925i,19926a-b
TI Partial hydrogenation of 1,4-butynediol. II. The role of calcium carbonate as a carrier of the palladium catalyst
AU Fukuda, Tosao
CS Yokohama Natl. Univ.
SO Bull. Chem. Soc. Japan (1958), 31, 343-7
DT Journal
LA Unavailable
AB cf. C.A. 52, 18199d. The poisoning effects of Pb(OAc)2 (I), piperidine, and quinoline (II) on the hydrogenation of 1,4-butynediol (III) and 1,4-butenediol over various Pd catalysts are given. Catalyst carriers studied were CaCO3, BaCO3, Al2O3, BaSO4, and C. Partial hydrogenation of III can be achieved with **PdBaCO3** poisoned by both I and II. CaCO3 as carrier seems to suppress polymerization accompanying hydrogenation, but does not increase catalytic activity or selectivity of the catalyst.

=>

L14 ANSWER 7 OF 11 CAPLUS COPYRIGHT 2002 ACS
AN 1958:113107 CAPLUS
DN 52:113107
OREF 52:19925i,19926a-b
TI Partial hydrogenation of 1,4-butynediol. II. The role of calcium carbonate
as a carrier of the palladium catalyst
AU Fukuda, Tosao
CS Yokohama Natl. Univ.
SO Bull. Chem. Soc. Japan (1958), 31, 343-7
DT Journal
LA Unavailable
AB cf. C.A. 52, 18199d. The poisoning effects of Pb(OAc)2 (I), piperidine, and quinoline (II) on the hydrogenation of 1,4-butynediol (III) and 1,4-butenediol over various Pd catalysts are given. Catalyst carriers studied were CaCO3, BaCO3, Al2O3, BaSO4, and C. Partial hydrogenation of III can be achieved with **PdBaCO3** poisoned by both I and II. CaCO3 as carrier seems to suppress polymerization accompanying hydrogenation, but does not increase catalytic activity or selectivity of the catalyst.

```
     (FILE 'HOME' ENTERED AT 14:23:32 ON 20 NOV 2002)

     FILE 'CAPLUS, USPATFULL' ENTERED AT 14:23:42 ON 20 NOV 2002
L1             0 S PD/MGCO3
L2            50 S PALLADIUM (P) MAGNESIUM CARBONATE
L3        337656 S HYDROGENAT?
L4            11 S L2 AND HYDROGENAT?
L5             0 S L4 AND ZSM5-NH4
L6             2 S L4 AND BARIUM CARBONATE
L7             9 S L4 NOT L6

     FILE 'STNGUIDE' ENTERED AT 14:31:07 ON 20 NOV 2002
L8             0 S PDMGCO3
L9             0 S 1,4-BUTYNEDIOL (P) 1,4-BUTENEDIOL (P) PALLADIUM

     FILE 'CAPLUS, USPATFULL' ENTERED AT 14:36:28 ON 20 NOV 2002
L10           10 S 1,4-BUTYNEDIOL (P) 1,4-BUTENEDIOL (P) PALLADIUM
L11            9 S 1,4-BUTYNEDIOL (P) 1,4-BUTENEDIOL (P) PLATINUM
L12            1 S L11 NOT L10
L13            1 S PTCACO3

     FILE 'STNGUIDE' ENTERED AT 14:48:03 ON 20 NOV 2002

     FILE 'CAPLUS, USPATFULL' ENTERED AT 14:50:45 ON 20 NOV 2002
L14           11 S PDBACO3
L15            0 S PDMGCO3
L16            0 S PTMGCO3
L17            0 S PTBACO3
L18            1 S PTCACO3
L19         1685 S LINDLAR? CATALYST
L20          791 S L19 AND PALLADIUM
L21          259 S L20 AND PLATINUM
L22          228 S L21 AND CARBONATE
L23           79 S L22 AND BARIUM
L24           70 S L23 AND MAGNESIUM
L25           60 S L24 AND CALCIUM
L26           53 S L25 AND HYDROGENAT?
L27           30 S L26 AND SUPPORT?
L28            4 S L27 AND ?BUTYNEDIOL
L29           26 S L27 NOT L28
L30           26 DUP REM L29 (0 DUPLICATES REMOVED)

     FILE 'STNGUIDE' ENTERED AT 15:06:51 ON 20 NOV 2002
L31            0 S PD-ZSM5

     FILE 'CAPLUS, USPATFULL' ENTERED AT 15:10:11 ON 20 NOV 2002
L32           16 S PD-ZSM5
L33            4 S L32 AND HYDROGENAT?
L34            1 S NH4-ZSM5
L35            1 S PD (P) ZSM5 (P) AMMONIUM
L36            0 S PDNH4-ZSM5
L37            0 S ZSM5-NH4
L38            5 S AMMONIUM ZSM5
L39            4 S L33 AND PALLADIUM
```

Although this work demonstrates the absence of Ph migration, a mechanism via II with H migration is a strong possibility and will be studied.

L7 ANSWER 9 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1959:1618 CAPLUS
DN 53:1618
OREF 53:196g-i
TI The **hydrogenation** of acetylene to ethylene
AU Shcheglov, N. I.; Sokol'skii, D. V.
SO Trudy Inst. Khim. Nauk, Akad. Nauk Kazakh. S.S.R. (1958), 2, 150-7
DT Journal
LA Unavailable
AB The process of selective **hydrogenation** of C2H2 (I) in the presence of Pd has been investigated and it was established that **PdCaCO3**, with additions of Pb, is an active **catalyst** which possesses good selective properties. For a 1:2 mixt. of I and H the max. yield of C2H4 (II) is 99%, calcd. on the amt. of I introduced, and for a 1:1 mixt. the yield is 90%, also calcd. on the amt. of I introduced, and up to 100% when calcd. on the amt. of I taking part in the reaction. The **catalyst** preserves its activity for a rather long time, in particular with initial mixts., in which the vol. I is relatively smaller than the vol. H. The deactivated **catalyst** easily recovers its activity when air is blown on it. Addn. of an inert gas to the initial mixt. increases the time of service of the **catalyst** but lowers somewhat the yield of II. Under the same conditions the **hydrogenation** of I is relatively more complete in the vapor phase than in the liquid phase, owing, apparently, to a better contact of I and H with the **catalyst**.

L7 ANSWER 10 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1957:86083 CAPLUS
DN 51:86083
OREF 51:15622f-i
TI Reduction of steroid peroxides
IN Laubach, Gerald D.
PA Chas. Pfizer & Co., Inc.
DT Patent
LA Unavailable
FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 2794033		19570528	US	

AB 11,14-Steroid peroxides are selectively reduced to compds. having OH groups in the nucleus at the same positions by **hydrogenation** in the presence of a Raney nickel **catalyst** or of a poisoned or deactivated palladium **catalyst**. The process is especially useful when a nuclear double bond is present in the 6,7-position as well as in the 8,9-position, since the reduction leaves the 8,9-double bond unchanged. **PdCaCO3** carrier is deactivated with Pb (5% Pd-4% Pb) and satd. with H. A soln. of 0.472 g. isodehydroergosteryl acetate peroxide (I), m. 157.0-8.0.degree., in 30 ml. EtOAc is hydrogenated over 0.2 g. of this **catalyst** at room temp. under 1 atm. H. H absorption ceases abruptly at the end of 2 hrs. after 25.2 ml. H has been taken up. The mixt. filtered, the filtrate concd. to dryness, and the residue recrystd. from Et2O-petr. ether gives the 6,7,8,9-nuclearly diunsatd. 11,14-dihydroxylated steroid, m. 158.6-62.2.degree.. Further recrystn. from MeOH gives a sample m. 157.4-60.0.degree., .epsilon.272 3340. A soln. of 0.234 g. I in 12 ml. anhyd. peroxide-free dioxane is

hydrogenated over 0.750 g. Raney Ni at room temp. and atm. pressure. After about 3 hrs. the H uptake is 24.5 ml. and absorption ceases. The mixt. is filtered and concd. under vacuum to an oily white solid which on trituration with petr. ether yields 0.091 g. solid, m. 144.4-50.6.degree..
The product is the 8,9-nuclearly monounsatd. 11,14-dihydroxylated deriv. of isoergosterol, .epsilon.248 1730.

L7 ANSWER 12 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1956:24142 CAPLUS
DN 50:24142
OREF 50:4928h-i,4929a-b
TI Tertiary triatomic alcohols of the acetylenic series and their transformations. VII. **Hydrogenation** of 2,3,6-trimethyl-4-heptyne-2,3,6-triol, 3,4,7-trimethyl-5-octyne-3,4,7-triol, 2-methyl-5-(1-hydroxycyclohexyl)-3-hexyne-2,5-diol, and 2,4-bis(1-hydroxycyclohexyl)-3-butyn-2-ol
AU Nikitin, V. I.; Timofeeva, I. M.
SO Zhur. Obshchei Khim. (1955), 25, 1334-43
DT Journal
LA Unavailable
AB cf. C.A. 50, 3253g. Pt and Pd **catalysts** cause the **hydrogenation** of acetylenic tertiary glycerols to the corresponding ethylenic alcs., yielding apparently the cis isomers. The **hydrogenation** curves over Pt or Pd have similar character in this group of compds., although the reaction rate over Pt is somewhat greater. Neither **PdCaCO3** nor PtO2 is capable of effecting **hydrogenation** of these compounds to the satd. analogs. In AcOH the Pt **catalyst** causes further absorption of H by the ethylenic derivs. but the reaction takes place at the expense of replacement of HO groups. 2,3,6-Trimethyl-4-heptyne-2,3,6-triol, b2.5 122.degree., m. 82.degree., hydrogenated in MeOH over PtO2 at normal conditions to 90% corresponding heptene deriv., m. 116-17.degree., also formed over Pd, and identified as cis-2,3,6-trimethyl-4-heptene-2,3,6-triol. 3,4,7-Trimethyl-5-octyne-3,4,7-triol, b2 118-19.degree., nD20 1.4794, similarly hydrogenated to the corresponding octene analog, b2 117-18.degree., nD20 1.4774, d20 1.0051. The reaction in AcOH over PtO2 gave a range of products, b3 83-97.degree., all fractions showing a decidedly decreased no. of HO groups from the initial 3. 2-Methyl-5-(1-hydroxycyclohexyl)-3-hexyne-2,5-diol, b3 151-5.degree., m. 87-8.degree., hydrogenated in MeOH over PtO2 to cis-2-methyl-5-(1-hydroxycyclohexyl)-3-hexene-2,5-diol. m. 102-3.degree., the same being formed over Pd. 2,4-Bis(1-hydroxycyclohexyl)-3-butyn-2-ol, m. 107-8.degree., hydrogenated over Pd or PtO2 in MeOH to cis-2,4-bis(1-hydroxycyclohexyl)-3-buten-2-ol, m. 111-12.degree..

=>

L7 ANSWER 1 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1967:482313 CAPLUS
DN 67:82313
TI 3-Aminoestra-1,3,5(10),8(9),14-pentaen-17-ones
IN Pappo, Raphael
PA Searle, G. D., and Co.
SO U.S., 7 pp.
CODEN: USXXAM
DT Patent
LA English
FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI US 3325481		19670613	US	19650930

GI For diagram(s), see printed CA Issue.

AB 2-Methyl-2-[(6-pyrrolidino-1-naphthylidene)ethyl]cyclopentane-1,3-dione (8.67 parts) with 0.375 part p-MeC6H4SO3H in 198 parts C6H6 under reflux 1 hr. gave 3-pyrrolidinoestra-1,3,5(10),8(9),14-pentaen-17-one (I), m. 173-5.degree.. **Hydrogenation** of 2 parts I in 200 parts 20% pyridine in C6H6 with 2 parts 5% **PdCaCO3 catalyst** at atm. pressure afforded 3-pyrrolidinoestra-1,3,5(10),8(9)-tetraen-17-one (II), m. 181-5.degree.. Redn. of 2 parts I in 18 parts tetrahydrofuran (THF) with 1.2 parts LiAlH4 in 13.5 parts THF at room temp. 7 hrs. yielded 3-pyrrolidinoestra-1,3,5(10),8(9),14-pentaen-17.beta.-ol (III), m. 188-90.degree.. **Hydrogenation** of 1.2 parts III in 100 parts 20% pyridine in C6H6 with 1 part 5% Pd-CaCO3 at atm. pressure 3 hrs. afforded 3-pyrrolidinoestra-1,3,5(10),8(9)-tetraen-17.beta.-ol (IV), m. 144-9.degree.. Alternate-LiAlH4 redn. of II at room temp. 6 hrs. gave IV. A mixt. of 31.36 parts 2-methyl-2-[[6-(dimethylamino)-1-naphthylidene]-ethyl]-cyclopentane-1,3-dione (IVa), 1.57 parts p-MeC6H4SO3H.H2O and 827 parts C6H6 under reflux 75 min. gave 3-(dimethylamino)estra-1,3,5(10),8(9),14-pentaen-17-one (V), m. 183-5.5.degree.. LiAlH4 redn. of V gave 3-(dimethylamino)estra-1,3,5(10),8(9),14-pentaen-17.beta.-ol (VI), m. 142-4.5.degree. (Et2O). **Hydrogenation** of V for 2 hrs. gave the -1,3,5(10),8(9)-tetraen-17-one (VII), m. 174-8.degree. (Me2CO-EtOH), which on LiAlH4 redn. afforded 3-(dimethylamino)estra-1,3,5(10),8(9)-tetraen-17.beta.-ol (VIII), m. 157-60.5.degree. (Et2O). **Hydrogenation** of VI also gave VIII. Reaction of 1.32 parts VII in 11.4 parts C6H6 with 1.22 parts camphorsulfonic acid, 3.9 parts CH(OMe)3, and 10.4 parts MeOH under N at room temp. 1 hr. yielded 3-(dimethylamino)estra-1,3,5(10),8(9)-tetraen-17-one 17-dimethyl ketal (IX), m. 75-80.degree. (pentane). VII with CH(OEt)3 gave the diethyl ketal, an oil. Acetylation of 1 part VI with 8 parts Ac2O in 10 parts pyridine at room temp. 16 hrs. gave the 17-acetate (X) of VI, m. 87-90.degree. (MeOH), which on **hydrogenation** gave the 17-acetate of VII. Addn. of 2.86 parts VI in 45 parts CHCl3 to 3.57 parts (+)-dibenzoyltartaric acid in 49 parts Et2O, reaction 5 hrs. at room temp., and decantation gave the amine-salt, m. 187-9.degree. (iso-PrOH). Dissoln. in MeOH, addn. of excess 5% aq. NaOH, and C6H6 extn. afforded (-)-VI, m. 145-8.degree., [.alpha.]D -77.degree.. IVa (3.2 parts) in 83.6 parts C6H6 with 0.19 part (+)-camphorsulfonic acid at reflux 75 min. under N, addn. of aq. NaOH and washing gave (-)-V, [.alpha.]D -0.5.degree. (CHCl3). 2-methyl-2-(6-acetamido-1-naphthyliden)ethylcyclopentane-1,3-

dione (9 parts), 0.9 part p-MeC6H4SO3H.H2O and 198 parts C6H6 under reflux
30 min. using a water separator gave 3-acetamidoestra-1,3,5(10),8(9),14-pentaen-17-one (XI), m. 207-10.degree.. Redn. of 2.68 parts XI in 145 parts THF with 4.86 parts LiAl(OBu-tert)3H in 72 parts THF under N at room
temp. 6.5 hrs. gave 3-acetamidoestra-1,3,5(10),8(9),14-pentaen-17.beta.-ol monohydrate (XII), m. 120-40.degree. and 218-231.degree.. **Hydrogenation** of 1.82 parts XI in 200 parts 20% pyridine in C6H6 with 1.82 parts 5% Pd-CaCO3 for 5 hrs. at room temp. and atm. pressure afforded 3-acetamidoestra-1,3,5(10),8(9)-tetraen-17-one (XIII), m. 178-189.degree.. Similarly, **hydrogenation** of XII gave the corresponding tetraene (XIV), m. 247-52.degree.. Redn. of 9.41 parts XIII
in 1064 parts EtOH with 9.41 parts NaBH4 in 380 parts H2O under N 2 hrs. at room temp. gave XIV.

L7 ANSWER 4 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1962:52931 CAPLUS
DN 56:52931
OREF 56:9966b-d
TI 1,8-Dialkoxy-1,3,5,7-octatetraenes
IN Meister, Herbert
PA Chemische Werke Huels A.-G.
DT Patent
LA Unavailable

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 1108207			DE	19581212

AB The title comps. were prepd. by partial **hydrogenation** of 1,8-dialkoxy-1,7-octadiene-3,5-diynes, obtainable as described in Ger. 1,015,788. A soln. of (MeOCH: CHC.tplbond.C)2 10 in MeOH 10 was hydrogenated at a low const. temp. after addn. of Lindlar **catalyst** (**PdCaCO3** + Pb) 2, quinoline 1, and hydroquinone 0.1 part. The crystd. product, (MeOCH:CHCH:CH)2 (I), was dissolved by heating under N on
a water bath, the **catalyst** filtered off, the filtrate was cooled, and the product filtered off under suction in a N atmosphere to give 66.3% I, m. 126-8.degree.. Similarly were prepd.: (EtOCH:CHCH:CH)2, m. 60-1.degree., 68.5%, and (iso-PrOCH: CHCH:CH)2, m. 72-4.degree., 68.5%.
I was also prepd. by oxidative dimerization of MeOCH:CHC.tplbond.CH and subsequent partial **hydrogenation** in a 23% yield.

L7 ANSWER 5 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1961:112033 CAPLUS
DN 55:112033
OREF 55:21072c-i,21073a-i,21074a
TI Derivatives of podocarpic acid. IV. Reduction of the aromatic ring
AU Bible, Roy H., Jr.; Burtner, Robert R.
CS G. D. Searle & Co., Chicago, IL
SO J. Org. Chem. (1961), 26, 1174-80
DT Journal
LA Unavailable
AB cf. CA 55, 4453d. **Hydrogenation** of the aromatic ring of podocarpic acid (I) gave the trans-anti-cis-perhydro deriv. (II). II was converted by a series of reactions, in which the rearrangement of a bromo ketone (IIa) during dehydrobromination was observed, to a compd. having the trans-anti-trans skeleton (III). III was prepd. from the Birch redn.

product of O-methylpodocarpinol (IV). The complete stereochemistry of the products was elucidated by interconversions and by a study of the spectra and optical rotations. Podocarpic acid (50 g.) in 250 ml. AcOH treated 2 hrs. under H and with 1.5 g. PtO2 at 60-76.degree., the mixt. stirred 5.5 hrs. at 875-820 lb./sq. in. H pressure with 1 g. fresh **catalyst**, the residue refluxed 2 hrs. with 50 g. KOH in 50 ml. H2O and 200 ml. MeOH, the mixt. acidified, and recrystd. gave 14.2 g. II, m. 234.5-6.0.degree., [.alpha.]D 23.degree. (unless otherwise noted all rotations detd. in 1% alc.). The 23 g. of material remaining in the mother liquor gave 3.3 g. deoxyperhydropodocarpic acid, m. 136-71.degree., [.alpha.]D 52.degree.. II acetate m. 134.5-6.0.degree., [.alpha.]D -11.degree.. II with Me2SO4 and NaOH gave Me trans-anti-cis-perhydropodocarpate (V), glass, b0.15 154.degree., [.alpha.]D 31.degree.. Methylation of II acetate gave acetate of V, m. 82-4.degree., [.alpha.]D -1.degree.. II (100 g.) in 40 ml. Me2CO oxidized with 150 ml. 8N CrO3 gave 93.5 g. 4.beta.-carboxy-4.alpha., 10.beta.-dimethyl-trans-anti-cis-perhydro-12-phenanthrone (trans-anti-cis-tetradecahydro-1.alpha.,4a.beta.-dimethyl-6-oxo-1.beta.-phenanthrenecarboxylic acid) (VI), m.167.5-74.degree., [.alpha.]D 35.degree.. Methylation of VI with Me2SO4 and NaOH gave 4.beta.-methoxycarbonyl-4.alpha.,10.beta.-dimethyl-trans-anti-cis-perhydro-12-phenanthrone (VII), m. 110-13.degree., or m. 120-1.5.degree., [.alpha.]D 41.degree.. N-Bromosuccinimide (8.81 g.) exposed to diffused sunlight 0.5 hr. with 14.5 g. VII in 70 ml. CCl4 gave 6.7 g. 4.beta.-methoxycarbonyl-4.alpha.,10.beta.-dimethyl-11.alpha.-bromo-trans-anti-cis-perhydro-12-phenanthrone (VIII), m. 152-3.degree. (hexane). **Hydrogenation** of the material in the mother liquor from VIII over 5% **PdCaCO3** in alc. at 25.degree. gave 4.9 g. VII. VIII (1.79 g.) and 6 ml. 48% HBr in 60 ml. AcOH left 48 hrs. at room temp. gave 0.210 g. equatorial bromo ketone, m. 143.5-7.0.degree., [.alpha.]D 59.degree.. VIII (4.31 g.) refluxed 0.5 hr. with 50 ml. collidine under N gave a yellow residue. The residue refluxed 35 min. in 200 ml. C6H6 with basic Al2O3 gave 0.52 g. 5.beta.-methoxycarbonyl-4.alpha.,10.beta.-dimethyl-trans-anti-trans-1,2,3,4,5.alpha.,6,7,8.beta.,9.alpha.,10,11,12-dodecahydro-12-phenanthrone (IX), blades, m. 126.5-9.0.degree. (aq. MeOH), [.alpha.]D 72.degree.. VIII (6.7 g.), 1.34 g. LiCl, and 1 g. Li2CO3 refluxed 6 hrs. in 142 ml. HCONMe2 gave 1.45 g. IX. IX (0.3 g.) hydrogenated in alc. over 0.03 g. 5% Pd-C at room temp. gave 0.16 g. 4.beta.-methoxycarbonyl-4.alpha.,10.beta.-dimethyl-trans-anti-trans-perhydro-12-phenanthrone (X), m. 116.5-21.5.degree. (aq. Me2CO), [.alpha.]D 48.degree. (c 0.5, alc.). Redn. of 5 g. II in 200 ml. Et2O during 4 days at room temp. with 3 g. LiAlH4 gave 1.8 g. II and 1.2 g. 4.beta.-hydroxymethylene-4.alpha.,10.beta.-dimethyl-trans-anti-cis-perhydro-12-phenanthrol, m. 120-3.degree., [.alpha.]D -52.degree.. VIII (10 g.) in 100 ml. CCl4 brominated at room temp. with 12.2 g. N-bromosuccinimide gave 1.44 g. 4.beta.-methoxycarbonyl-4.alpha.,10.beta.-dimethyl-11.alpha.,13.alpha.-dibromo-trans-anti-cis-perhydro-12-phenanthrone (XI), m. 162-4.5.degree., [.alpha.]D 5.degree.. XI (0.5 g.) in 6 ml. HCONMe2 refluxed 1.5 hrs. with 0.282 g. LiCl gave 0.27 g. Me podocarpate, m. 204.5-8.0.degree. (aq. MeOH). VI (0.5 g.) in 25 ml. PrOH refluxed during the addn. of 2.5 g. Na, then refluxed 1 hr., and the product purified gave 0.33 g. 4.beta.-carboxy-4.alpha.,10.beta.-dimethyl-trans-anti-cis-perhydro-12.alpha.-phenanthrol (XII), m. 253-6.degree., [.alpha.]D 52.degree.. VI (5.1 g.) and 0.74 g. NaOH in 53 ml. alc. left 40 hrs. at room temp. with 2.8 g. NaBH4 gave 4.98 g. mixt. of 70% II and

30% XII. Li wire (10 g.) added in 12 min. to 20 g. IV in 250 ml. Me3COH, 250 ml. tetrahydrofuran, and 600 ml. NH3, the mixt. left 1 hr., 50 ml. MeOH added, the mixt. evapd., and distd. gave 19.3 g. residue, which recrystd. gave 4.beta.-hydroxymethylene-4.alpha.,10.beta.-dimethyl-12-methoxy-1,2,3,4,5.alpha.,6,7,10,11,12-decahydrophenanthrene (XIII), m. 100-3.degree. (hexane). Crude XIII in 153 ml. MeOH contg. 10.2 ml. 12M HCl and 6.8 ml. H2O left 2 hrs. at room temp. and the 18 g. of crude product treated with 18 g. Girard reagent T gave 6 g. nonketonic material and 7.4 g. 4.beta.-hydroxymethylene-4.alpha.,10.beta.-dimethyl-1,2,3,4,5.alpha.,6,7,8.beta.,10,12,13,14-dodecahydro-12-phenanthrone (XIV), m. 111-12.degree. (EtOAc); semicarbazone m. 255.degree. (decompn.).

The crude nonketonic fraction was chromatographed over silica gel to give 4.5 g. 4.beta.-hydroxymethylene-4.alpha.,10.beta.-dimethyldodecahydrophenanthrene, m. 108-9.degree. (80% MeOH). XIV (10.6 g.) oxidized in 500 ml. Me2CO with 23 ml. N CrO3H2SO4 gave 10 g. crude aldehyde. This crude aldehyde (10 g.) in 100 ml. AcOH at 15-20.degree. treated with 3.2 g. CrO3 in 66% AcOH and left overnight gave another crude aldehyde. This aldehyde (7 g.) was methylated with Me2SO4 and NaOH to give 5.5 g. 4.beta.-methoxycarbonyl-4.alpha.,10.beta.-dimethyl-1,2,3,4,5.alpha.,6,7,8.beta.,10,12,13,14-dodecahydro-12-phenanthrone, m. 116-18.degree. (MeOH). XIV (2 g.) in 25 ml. Me3COH, 25 ml. tetrahydrofuran, and 60 ml. NH3 reduced 3 hrs. with 1 g. Li gave 2 g. crude 4.beta.-hydroxymethylene-4.alpha.,10.beta.-dimethyl-trans-anti-trans-perhydro-12-phenanthrone (XV), yellow glass. Acetylation of XV gave the acetate, m. 114.5-16.0.degree. (hexane), [.alpha.]D 13.5.degree.. Sapon. of this acetate gave XV, m. 105.degree. (EtOAc), [.alpha.]D 18.8.degree.. XV (5.3 g.) in 50 ml. AcOH stirred 20 min. at 15-20.degree. with addn. of 3 g. CrO3 in 2 ml. H2O and 8 ml. AcOH, stirred a further 20 min., and dild. with H2O gave 3 g. crude X. XV in Me2CO with CrO3-H2SO4 gave the crude oxto aldehyde and further oxidn. with CrO3 in AcOH gave X. Crude X (2.22 g.) methylated with Me2SO4 and NaOH in 50% MeOH and extd. with CHCl3 gave 0.65 g. III, m. 119-20.degree., [.alpha.]D 51.degree. (alc.). X (3 g.) in 100 ml. alc. contg. 0.8 g. NaOH refluxed 2 hrs. with 1.8 g. NaBH4 in 25 ml. 80% alc., acidified, dild. with H2O, and recrystd. gave 1 g. 4.beta.-carboxy-4.alpha.,10.beta.-dimethyl-trans-anti-trans-perhydro-12.beta.-phenanthrol (XVI), spikes, m. 248-50.degree. (EtOAc), [.alpha.]D 41.4.degree.. Crude X with Na in PrOH gave XVI. Acetylation of 530 mg. crude XVI gave 436 mg. acetate, m. 152-4.degree., [.alpha.]D 5.5.degree..

K (35 g.) in 800 ml. Me3COH dild. with 200 ml. PhMe, chilled to 5.degree., satd. with C2H2, 25 g. XV in 200 ml. PhMe added all at once, the mixt. treated a further 5 hrs. with C2H2 gave 3.03 g. 4.beta.-hydroxymethylene-4.alpha.,10.beta.-dimethyl-12.xi.-ethynyl-trans-anti-trans-perhydro-12.xi.-phenanthrol (XVII), m. 217-19.degree., [.alpha.]D 3.5.degree.. The mother liquors afforded 22 g. oily material and chromatography of this product on silica gel gave 4.33 g. isomeric product, m. 165.degree., [.alpha.]D 39.5.degree.. The 80% C6H6-20% EtOAc fraction gave 3.64 g. XVII. XVII (2.95 g.) in 40 tetrahydrofuran added during 5 min. to 0.15 mole MeMgBr in tetrahydrofuran, the mixt. refluxed 24 hrs., the suspension poured onto 500 ml. 5% H2SO4, partially evapd., the crude acid taken up in 140 ml. H2O

contg. 3 ml. diethanolamine at 65.degree., filtered through Celite, and the filtrate acidified gave 1.52 g. crude 4.beta.-hydroxymethylene-

4.alpha.,10.beta.-dimethyl-12.xi.-carboxyethynyl-trans-anti-trans-perhydro-12.xi.-phenanthrol, which was used without further purification. This crude acetylenic acid (1.5 g.) in 100 ml. alc. hydrogenated at atm. pressure, the filtered soln. treated with 4 ml. 10% NaOH, evapd. to 25 ml., and treated with 6N HCl gave 0.8 g. pure 4.beta.-hydroxymethylene-4.alpha.,10.beta.-dimethyl-12.xi.-carboxyethyl-trans-anti-trans-perhydro-12.xi.-phenanthrol .alpha.-lactone (XVIII), m. 179-80.degree. (EtOAc), [.alpha.]D 17.degree.. Carboxylation of 4.3 g. of the acetylenic alc. isomeric with XVII gave 1.28 g. isomer of XVIII, plates. m. 235-40.degree.
(EtOAc), [.alpha.]D 23.6.degree.. The infrared [spectra were given for many of the above compds.

L7 ANSWER 7 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1959:56162 CAPLUS
DN 53:56162
OREF 53:10080d-h
TI The catalytic **hydrogenation** of 3-phenyl-1-butene-2-C14
AU Bonner, Wm. A.; Stehr, Charles E.; do Amaral, Jefferson R.
CS Stanford Univ., Stanford, CA
SO J. Am. Chem. Soc. (1958), 80, 4732-6
DT Journal
LA Unavailable
AB Partial racemization of D(-)MeCH(Ph)CH:CH2 (I) during **hydrogenation** (D. J. Cram, ibid., 74, 5518 (1952)) does not occur via a hypothesized Ph migration in an intermediate MeCH(Ph)(CHMe (II). I-2-C14 was prepd. starting from AcPh and BrC14H2CO2Me via a Reformatzkii reaction to give 30.1 g. MeC(Ph):C*HCO2Me, b18 136-8.degree., hydrogenating in vacuo with PtO2 to 32.5 g. MeCH(Ph)C*H2CO2Me n19.5D 1.4972, and treating with LiAlH4, and PB3 to give 31.2 g. MeCH(Ph)C*H2Br, b19 123-4.degree. n21.5D 1.5341; this was converted to 26.7 g. Me2NH deriv. by heating with 38 g. Me2NH and 64 ml. purified dioxane in a bomb tube 12.5 hrs. at 100.degree., and oxidized to the crude emine oxide with 30% H2O2, followed by destruction of excess oxidant by catalase from an aq. ext. of avocado skins. Pyrolysis under 5 mm. N at 90-140.degree., dissocn. in C5H12, washing with dil. HCl and NaOH, drying, and distg. gave
8.7 g. chromatographically pure I-2-C14 b19 66-8.degree., n23.5D 1.5043. The label content at C-1 was detd. (zero) by HIO4 and KMnO4 oxidation to H2CO and assay for the dimedone deriv., m. 189.degree.. The result was confirmed by ozonization, LiAlH4 reduction to 97.2% MeCH(Ph)C*H2OH (III), and assay of the acid 3-nitrophthalate, m. 143-3.5.degree. (PhMe). To analyze the radioactivity of III, 0.76 g. was cleaved to PhEt by refluxing
6 hrs. in abs. EtOH with 4 g. Raney Ni, filtering and rinsing the **catalyst**, dilg. with 140 ml. H2O, extg. with C5H12, drying over P2O5 and filtering; fractionation through a column was followed by vapor-liquid partition chromatography; radioactive assay of the PhEt (inactive) was made by conversion to the 2,4-diacetylamino deriv., m. 224.degree.. Catalytic **hydrogenation** of I was carried out under several conditions (PtO2, Ni, **PdCaCO3**, Pd-C) with uptake of 98.8-100.5% H and 77-89% yields of MeCH(Ph)Et (IV) n22.5D 1.4878; in all cases Ph migration was below 1%, as found by oxidation of IV to BzOH and radioactivity assay thereof. The oxidation was most satisfactory via AcPh
(90% yield with CrO3-HOAc) treated with NaOH and Cl gas to give 88% BzOH m. 122-2.5.degree. (vacuum sublimed), according to known procedures.

L7 ANSWER 1 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1967:482313 CAPLUS
DN 67:82313
TI 3-Aminoestra-1,3,5(10),8(9),14-pentaen-17-ones
IN Pappo, Raphael
PA Searle, G. D., and Co.
SO U.S., 7 pp.
CODEN: USXXAM
DT Patent
LA English
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 3325481		19670613	US	19650930

L7 ANSWER 2 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1967:473263 CAPLUS
DN 67:73263
TI Determination of double bonds in side chains of polyfluoroaromatic compounds
AU Burlaka, V. P.; Diakur, L. N.
CS Novosibirsk. Inst. Org. Khim., Novosibirsk, USSR
SO Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk (1967), (1), 130-5
CODEN: IZSKAB
DT Journal
LA Russian

L7 ANSWER 3 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1966:473095 CAPLUS
DN 65:73095
OREF 65:13588f-h,13589a
TI Synthesis of 3-alkyl and 3-acylcatechol
AU Hanafusa, Terukiyo; Yukawa, Yasuhide
SO Mem. Inst. Sci. Ind. Res., Oska Univ. (1966), 23, 85-96
DT Journal
LA English

L7 ANSWER 4 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1962:52931 CAPLUS
DN 56:52931
OREF 56:9966b-d
TI 1,8-Dialkoxy-1,3,5,7-octatetraenes
IN Meister, Herbert
PA Chemische Werke Huels A.-G.
DT Patent
LA Unavailable

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	DE 1108207			DE	19581212

L7 ANSWER 5 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1961:112033 CAPLUS
DN 55:112033
OREF 55:21072c-i,21073a-i,21074a
TI Derivatives of podocarpic acid. IV. Reduction of the aromatic ring
AU Bible, Roy H., Jr.; Burtner, Robert R.
CS G. D. Searle & Co., Chicago, IL
SO J. Org. Chem. (1961), 26, 1174-80
DT Journal

LA Unavailable

L7 ANSWER 6 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1961:28083 CAPLUS
DN 55:28083
OREF 55:5585d-i,5586a-i,5587a-d
TI On steroids. LV. Bromination of 3.beta.-acetoxy-5.alpha.-androstan-16-one
AU Fajkos, J.; Joska, J.
CS Ceskoslov. akad. ved, Prague
SO Collection Czechoslov. Chem. Communs. (1960), 25, 2863-77
DT Journal
LA Unavailable

L7 ANSWER 7 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1959:56162 CAPLUS
DN 53:56162
OREF 53:10080d-h
TI The catalytic **hydrogenation** of 3-phenyl-1-butene-2-C14
AU Bonner, Wm. A.; Stehr, Charles E.; do Amaral, Jefferson R.
CS Stanford Univ., Stanford, CA
SO J. Am. Chem. Soc. (1958), 80, 4732-6
DT Journal
LA Unavailable

L7 ANSWER 8 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1959:11562 CAPLUS
DN 53:11562
OREF 53:2111h-i,2112a-i,2113a-i,2114a-b
TI Constellation analysis. II. Stereospecificity of reactions
AU Huckel, Walter; Maier, Martin; Jordan, Eberhard; Seeger, Wolfgang
CS Univ. Tubingen, Germany
SO Ann. (1958), 616, 46-81
DT Journal
LA Unavailable

L7 ANSWER 9 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1959:1618 CAPLUS
DN 53:1618
OREF 53:196g-i
TI The **hydrogenation** of acetylene to ethylene
AU Shcheglov, N. I.; Sokol'skii, D. V.
SO Trudy Inst. Khim. Nauk, Akad. Nauk Kazakh. S.S.R. (1958), 2, 150-7
DT Journal
LA Unavailable

L7 ANSWER 10 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1957:86083 CAPLUS
DN 51:86083
OREF 51:15622f-i
TI Reduction of steroid peroxides
IN Laubach, Gerald D.
PA Chas. Pfizer & Co., Inc.
DT Patent
LA Unavailable
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 2794033		19570528	US	

L7 ANSWER 11 OF 22 CAPLUS COPYRIGHT 2002 ACS

AN 1956:82156 CAPLUS
DN 50:82156
OREF 50:15571c-i,15572a-e
TI Steroids. XXIII. Synthesis and configuration of the two stereoisomeric 3.beta.-hydroxy-16-acetylandrostanes
AU Fajkos, Jan; Sorm, Frantisek
CS Csl. akad. ved, Prague
SO Chem. Listy (1956), 50, 791-9
DT Journal
LA Unavailable

=> d l7 bib 12-22

L7 ANSWER 12 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1956:24142 CAPLUS
DN 50:24142
OREF 50:4928h-i,4929a-b
TI Tertiary triatomic alcohols of the acetylenic series and their transformations. VII. **Hydrogenation** of 2,3,6-trimethyl-4-heptyne-2,3,6-triol, 3,4,7-trimethyl-5-octyne-3,4,7-triol, 2-methyl-5-(1-hydroxycyclohexyl)-3-hexyne-2,5-diol, and 2,4-bis(1-hydroxycyclohexyl)-3-butyn-2-ol
AU Nikitin, V. I.; Timofeeva, I. M.
SO Zhur. Obshchei Khim. (1955), 25, 1334-43
DT Journal
LA Unavailable

L7 ANSWER 13 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1956:20138 CAPLUS
DN 50:20138
OREF 50:4182d-i,4183a-c
TI Steroids. XVIII. Cleavage of 16,17-epoxy derivatives of androstane
AU Fajkos, Jan
CS Czech. akad. ved
SO Collection Czechoslov. Chem. Communs. (1955), 20, 1478-83
DT Journal
LA English

L7 ANSWER 14 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1956:20137 CAPLUS
DN 50:20137
OREF 50:4182d-i,4183a-c
TI Steroids. XVIII. Cleavage of 16,17-epoxy derivatives of androstane
AU Fajkos, Jan
CS Czech. akad. ved, Prague
SO Chem. Listy (1955), 49, 1218-23
DT Journal
LA Unavailable

L7 ANSWER 15 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1956:12175 CAPLUS
DN 50:12175
OREF 50:2505b-f
TI Carotenoid syntheses. XVI. Stereoisomeric 1,3,7,12,16,18-hexaphenyloctadecanonaenes
AU v. Ziegler, H. H.; Eugster, C. H.; Karrer, P.
CS Univ. Zurich, Switz.
SO Helv. Chim. Acta (1955), 38, 613-38
DT Journal

LA German

L7 ANSWER 16 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1954:14849 CAPLUS
DN 48:14849
OREF 48:2749d-i,2750a-h
TI Steroids. XLIII. A ten-step conversion of progesterone to cortisone. The differential reduction of pregnane-3,20-diones with sodium borohydride
AU Mancera, O.; Ringold, Howard J.; Djerassi, Carl; Rosenkranz, G.; Sondheimer, Franz
CS Syntex, S.A., Mexico City, Mex.
SO J. Am. Chem. Soc. (1953), 75, 1286-90
DT Journal
LA Unavailable

L7 ANSWER 17 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1952:23428 CAPLUS
DN 46:23428
OREF 46:3984i,3985a-i,3986a-e
TI Syntheses in the carotenoid series. XXI. Condensation of carotenoid-ketones and aldehydes with diacetylene; another synthesis of .beta.-carotene
AU Inhoffen, Hans Herloff; Bohlmann, Ferdinand; Aldag, Hans Joachim; Bork, Siegfried; Leibner, Gerhard
CS Tech. Hochschule, Braunschweig, Germany
SO Ann. (1951), 573, 1-16
DT Journal
LA Unavailable

L7 ANSWER 18 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1951:32863 CAPLUS
DN 45:32863
OREF 45:5724d-h
TI Pentaenes
IN Isler, Otto
PA Hoffmann-La Roche Inc.
DT Patent
LA Unavailable
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 2540118		19510206	US	

L7 ANSWER 19 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1949:34187 CAPLUS
DN 43:34187
OREF 43:6194g-i,6195a-i,6196a-i,6197a-i,6198a-i,6199a-i,6200a-i,6201a-c
TI Cyclizing polymerization of acetylene. I. Cyclo-octatetraene
AU Reppe, Walter; Schichting, Otto; Klager, Karl; Toepel, Tim
SO Ann. (1948), 560, 1-92
DT Journal
LA Unavailable

L7 ANSWER 20 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1949:17439 CAPLUS
DN 43:17439
OREF 43:3374f-i,3375a-c
TI Volatile plant substances. LXXII. 4-p-Menthanol, m. 53.degree.
AU Naves, Yves R.
SO Helv. Chim. Acta (1948), 31, 1937-43

DT Journal
LA French

L7 ANSWER 21 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1945:17551 CAPLUS
DN 39:17551
OREF 39:2732i,2733a-h
TI Polyene series. XXI. Ethynylcarbinols from .alpha.,.beta.-unsaturated ketones: their anionotropic rearrangements and other reactions
AU Cymerman, J.; Heilbron, I. M.; Jones, E. R. H.
SO J. Chem. Soc. (1945) 90-4
DT Journal
LA Unavailable

L7 ANSWER 22 OF 22 CAPLUS COPYRIGHT 2002 ACS
AN 1941:11186 CAPLUS
DN 35:11186
OREF 35:1787i,1788a-i,1789a-h
TI Diene syntheses. XXXV. Synthetic experiments in the series of cantharidin, nor- and isocantharidins
AU Diels, Otto; Olsen, Sigurd
SO J. prakt. Chem. (1940), 156, 285-314
DT Journal
LA Unavailable

=>

7 ANSWER 1 OF 22 CAPLUS COPYRIGHT 2002 ACS
AB 2-Methyl-2-[(6-pyrrolidino-1-naphthylidene)ethyl]cyclopentane-1,3-dione (8.67 parts) with 0.375 part p-MeC6H4SO3H in 198 parts C6H6 under reflux 1 hr. gave 3-pyrrolidinoestra-1,3,5(10),8(9),14-pentaen-17-one (I), m. 173-5.degree.. **Hydrogenation** of 2 parts I in 200 parts 20% pyridine in C6H6 with 2 parts 5% **PdCaCO3 catalyst** at atm. pressure afforded 3-pyrrolidinoestra-1,3,5(10),8(9)-tetraen-17-one (II), m. 181-5.degree.. Redn. of 2 parts I in 18 parts tetrahydrofuran (THF) with 1.2 parts LiAlH4 in 13.5 parts THF at room temp. 7 hrs. yielded 3-pyrrolidinoestra-1,3,5(10),8(9),14-pentaen-17.beta.-ol (III), m. 188-90.degree.. **Hydrogenation** of 1.2 parts III in 100 parts 20% pyridine in C6H6 with 1 part 5% Pd-CaCO3 at atm. pressure 3. . . C6H6 under reflux 75 min. gave 3-(dimethylamino)estra-1,3,5(10),8(9),14-pentaen-17-one (V), m. 183-5.5.degree.. LiAlH4 redn. of V gave 3-(dimethylamino)estra-1,3,5(10),8(9),14-pentaen-17.beta.-ol (VI), m. 142-4.5.degree. (Et2O). **Hydrogenation** of V for 2 hrs. gave the -1,3,5(10),8(9)-tetraen-17-one (VII), m. 174-8.degree. (Me2CO-EtOH), which on LiAlH4 redn. afforded 3-(dimethylamino)estra-1,3,5(10),8(9)-tetraen-17.beta.-ol (VIII), m. 157-60.5.degree. (Et2O). **Hydrogenation** of VI also gave VIII. Reaction of 1.32 parts VII in 11.4 parts C6H6 with 1.22 parts camphorsulfonic acid, 3.9. . . in 10 parts pyridine at room temp. 16 hrs. gave the 17-acetate (X) of VI, m. 87-90.degree. (MeOH), which on **hydrogenation** gave the 17-acetate of VII. Addn. of 2.86 parts VI in 45 parts CHCl3 to 3.57 parts (+)-dibenzoyltartaric acid in. . . LiAl(OBu-tert)3H in 72 parts THF under N at room temp. 6.5 hrs. gave 3-acetamidoestra-1,3,5(10),8(9),14-pentaen-17.beta.-ol monohydrate (XII), m. 120-40.degree. and 218-231.degree.. **Hydrogenation** of 1.82 parts XI in 200 parts 20% pyridine in C6H6 with 1.82 parts 5% Pd-CaCO3 for 5 hrs. at room temp. and atm. pressure afforded 3-acetamidoestra-1,3,5(10),8(9)-tetraen-17-one (XIII), m. 178-189.degree.. Similarly, **hydrogenation** of XII gave the corresponding tetraene (XIV), m. 247-52.degree.. Redn. of 9.41 parts XIII in 1064 parts EtOH with 9.41. . .

L7 ANSWER 2 OF 22 CAPLUS COPYRIGHT 2002 ACS
AB In the **hydrogenation** of C:C double bonds in the side chains of polyfluoroaromatic compds., PtO2 in HOAc was not suitable for C6F5CH:CHCH:NNHCONH2 (I). . . also catalyzed H substitution for F on the ring. PtO2 in abs. EtOH was also unsatisfactory for II. Pd black, **PdCaCO3** and Pd-C were unsuitable because they gave less than quant. **hydrogenation** of the side chain. However, the use of Pd3B2 as the **catalyst** in EtOH and dioxane gives quant. **hydrogenation** of C:C double bonds in the side chain for I, II, C6F5CH:CHCHO, C6F5CH:CH2, and C6F5CH:CHCO2H. Pd3B2 in HOAc gave high values for I and II. Pd3B2 gave quant. side chain **hydrogenation** in either abs. EtOH or HOAc for 5,6,7,8-tetrafluorobenzobicyclo[2.2.2]octa triene (III); for the following derivs. of III: 1-Me, 2-Me, 1-MeO, 1,3,10-trimethyl; and. . .
ST AROMS POLYFLUORO **HYDROGENATION; HYDROGENATION** POLYFLUORO AROMS; PALLADIUM BORIDE **HYDROGENATION** AROMS; BICYCLOOCTATRIENES FLUOROBENZO; POLYFLUORO AROMS **HYDROGENATION**
IT **Hydrogenation**
(of side chains in polyfluoro aromatic compds.)

IT 653-34-9 719-60-8 5162-34-5 14111-43-4 14111-44-5 14519-84-7
15269-18-8 15269-19-9 15269-23-5 15269-24-6 15269-28-0
RL: RCT (Reactant)
(**hydrogenation** of)

L7 ANSWER 3 OF 22 CAPLUS COPYRIGHT 2002 ACS
AB . . . (1.4 g.), b0.02 180-90.degree., m. 57-8.degree. (petroleum ether). II proved identical to the redn. product of natural urushiol obtained by **hydrogenation** over 5% Pd-CaCO3 **catalyst**. Similarly prepd. were 3-n-hexylcatechol, b2 152-8.degree.; 3-n-dodecylcatechol, b0.3 165-9.degree., m. 49-51.degree.; 3-oleylcatechol, b0.01M 210-20.degree. (.alpha.-naphthylurethan deriv. m. 131-3.degree.); 3-decanoylcatechol, b0.002. . . 140-1.degree., uv absorption max. 266 m.mu., which gave a yellow color with Pb(OAc)2 and did not absorb H over 5% **PdCaCO3**. This was 2-methyl-8-hydroxychromanone and its spectrum showed ir absorption bands at 1665, 779, and 723 cm.-1

L7 ANSWER 4 OF 22 CAPLUS COPYRIGHT 2002 ACS
AB The title comps. were prepd. by partial **hydrogenation** of 1,8-dialkoxy-1,7-octadiene-3,5-diynes, obtainable as described in Ger. 1,015,788. A soln. of (MeOCH: CHC.tplbond.C)2 10 in MeOH 10 was hydrogenated at a low const. temp. after addn. of Lindlar **catalyst** (**PdCaCO3** + Pb) 2, quinoline 1, and hydroquinone 0.1 part. The crystd. product, (MeOCH:CHCH:CH)2 (I), was dissolved by heating under N on a water bath, the **catalyst** filtered off, the filtrate was cooled, and the product filtered off under suction in a N atmosphere to give 66.3%. . . 60-1.degree., 68.5%, and (iso-PrOCH: CHCH:CH)2, m. 72-4.degree., 68.5%. I was also prepd. by oxidative dimerization of MeOCH:CHC.tplbond.CH and subsequent partial **hydrogenation** in a 23% yield.

L7 ANSWER 5 OF 22 CAPLUS COPYRIGHT 2002 ACS
AB cf. CA 55, 4453d. **Hydrogenation** of the aromatic ring of podocarpic acid (I) gave the trans-anti-cis-perhydro deriv. (II). II was converted by a series of. . . 1.5 g. PtO2 at 60-76.degree., the mixt. stirred 5.5 hrs. at 875-820 lb./sq. in. H pressure with 1 g. fresh **catalyst**, the residue refluxed 2 hrs. with 50 g. KOH in 50 ml. H2O and 200 ml. MeOH, the mixt. acidified,. . . diffused sunlight 0.5 hr. with 14.5 g. VII in 70 ml. CCl4 gave 6.7 g. 4.beta.-methoxycarbonyl-4.alpha.,10.beta.-dimethyl-11.alpha.-bromo-trans-anti-cis-perhydro-12-phenanthrone (VIII), m. 152-3.degree. (hexane). **Hydrogenation** of the material in the mother liquor from VIII over 5% **PdCaCO3** in alc. at 25.degree. gave 4.9 g. VII. VIII (1.79 g.) and 6 ml. 48% HBr in 60 ml. AcOH. . .

=> d l7 kwic 6-11

L7 ANSWER 6 OF 22 CAPLUS COPYRIGHT 2002 ACS
AB . . . acetate treated with 0.3 ml. concd. H2SO4 in 5 ml. isopropenyl acetate, 15 ml. mixt. distd. in 2 hrs., more **catalyst** and solvent added, 35 ml. distillate collected over 2 hrs., the mixt. dild. with petr. ether and passed over Al2O3,. . . the mixt. with ice-cold 2% AcOH, and extg. the product with Et2O, prisms, m. 138-40.degree., [.alpha.]20D -38.5 .+-.1.degree. (c 2.6). **Hydrogenation** of III over Pd-CaCO3 in dioxane yielded 93% 3.beta.,16.beta.-diacetoxy-5.alpha.-

androstane (VII), m. 109.degree., [.alpha.]20D -8 .+-.1.degree. (c 1.42), showing that the reaction proceeded stereospecifically, since the **hydrogenation** product was identical with those obtained in 70%, 80%, and 63% yield, resp., by acetylating 3.beta.-acetoxy-5.alpha.-androstan-16.beta.-ol (VIII) with Ac2O in. . . or alternatively in the same way in 79% yield from VI, crystals, m. 152-3.degree. (MeOH), [.alpha.]20D 32 .+-.1.degree. (c 1.04). **Hydrogenation** of 100 mg. XII in EtOH with addn. of 2 portions of fresh **catalyst** at 6-hr. intervals gave 36 mg. 3.beta.,16.alpha.-diacetoxy-5.alpha.-androstane, m. 176.degree. (MeOH), [.alpha.]20D -34.2 .+-.1.degree. (c 1.14). XII (150 mg.) refluxed with. . . by allowing to stand

3.beta.-acetoxy-15.beta.-bromo-16.beta.,17.beta.-oxido-5.alpha.-androstane (XIX) with 40% HBr in CHCl3AcOH 18 hrs. at 30.degree.. IX (2 g.) hydrogenated over **PdCaCO3** in EtOH 10 hrs. and an addnl. 15 hrs. after addn. of fresh **catalyst** gave 800 mg. X, m. 198-9.degree. (MeOH), [.alpha.]20D -11.2 .+-.1.degree. (c 1.78), identical with the product obtained by the **hydrogenation** of 3.beta.,16.beta.-diacetoxy-15.beta.-bromo-17.alpha.-iodo-5.alpha.-androstane (XX) in 75% yield, and by acetylation of 15.beta.-bromo-5.alpha.-androstane-3.beta.,16.beta.-diol (XXI) in 78% yield. XXI, obtained in 90-mg. yield. . . MeOH 175 mg. 3.beta.-acetoxy-5.alpha.-androst-15-ene (XXII), m. 73-4.degree., [.alpha.]20D -53 .+-.1.degree. (c 1.74); MeOH solvate m. 43-5.degree.. XXII was identified by **hydrogenation** over PtO2 in AcOH to 88% 3.beta.-acetoxy-5.alpha.-androstane, m. 86-7.degree. (MeOH), [.alpha.]20D -8.2 .+-.1.degree. (c 0.98). XXII (60 mg.) refluxed with.

. -78 .+-.1.degree. (c 2.83). XXV (230 mg.) hydrogenated over 5% Pd-CaCO3 in EtOH 6 hrs. and, after addn. of fresh **catalyst**, an addnl. 16 hrs. gave 140 mg. 3.beta.,16.beta.-diacetoxy-17.alpha.-chloro-5.alpha.-androstane (XXVII), m. 136-7.degree. (EtOH), [.alpha.]20D -7 .+-.1.degree. (c 2.63), identical with the. . .

L7 ANSWER 7 OF 22 CAPLUS COPYRIGHT 2002 ACS
TI The catalytic **hydrogenation** of 3-phenyl-1-butene-2-C14
AB Partial racemization of D(-)MeCH(Ph)CH:CH2 (I) during **hydrogenation** (D. J. Cram, ibid., 74, 5518 (1952)) does not occur via a hypothesized Ph migration in an intermediate MeCH(Ph)(CHMe (II)..

. was cleaved to PhEt by refluxing 6 hrs. in abs. EtOH with 4 g. Raney Ni, filtering and rinsing the **catalyst**, dilg. with 140 ml. H2O, extg. with C5H12, drying over P2O5 and filtering; fractionation through a column was followed by. . . vapor-liquid partition chromatography; radioactive assay of the PhEt (inactive) was made by conversion to the 2,4-diacetylamino deriv., m. 224.degree.. Catalytic **hydrogenation** of I was carried out under several conditions (PtO2, Ni, **PdCaCO3**, Pd-C) with uptake of 98.8-100.5% H and 77-89% yields of MeCH(Ph)Et (IV) n22.5D 1.4878; in all cases Ph migration was. . .

L7 ANSWER 8 OF 22 CAPLUS COPYRIGHT 2002 ACS
AB The steric course of the reductions of numerous alicyclic ketones, induced by various **catalysts** used in **hydrogenation** was studied. Special reference is made to the configurations and constellations of the resulting alcs. In mixts. of the phenylurethans.

. mixt., b15 112-15.degree., contg. 60% I. III (7.5 g.) in 90 cc. MeOH hydrogenated at 20.degree./740 mm. with 3 g. **PdCaCO3** (contg. 40 mg. Pd) added 90% of the calcd. H to form cyclopenlylcyclopentanone (IV) within 8 min. III (199 g.). . . and 1.7 g. still residue, 32.2 g. I-II

mixt. contg. 56% I. Another similar run using a less active Pt **catalyst** gave a mixt. contg. 51% I. Using 0.5 g. PtO2, 7.7 g. IV in 80 cc. EtOH was hydrogenated 100. . . into 1-cyclohexenyl-2-cyclohexanone (V), n20D 1.5063. 2-(1-Cyclohexylidene)cyclohexanone (VI), m. 55.degree. (80% MeOH), was prepd. by Reese's method (C.A. 37, 30626). Rapid **hydrogenation** of either 8.9 g. V or VI was effected in 90 cc. MeOH using 3 g. Pd-CaCO3 (contg. 40 mg.. . . 133-4.degree., n20D 1.4893, in good (but unspecified) yield, when large amts. of V or VI were to be hydrogenated, the **catalyst** was reactivated by air. VII (10 g.) hydrogenated in AcOH-HCl with Pt black, followed by sapon. of esters gave a. . . S and K of various mixts, of pure phenylurethans of VIIIa and VIIIb are given together with a m.p. diagram. **Hydrogenations** of VII to form the mixt. of alcs. was also effected with PtO2 in AcOH, giving 70% VIIIa, and with. . . 1.4647, contg. about 80% cis form (XVa), as gaged from the p-nitrobenzoate, S 32.4.degree., M 40.2.degree., and K 45.1.degree.. The **hydrogenation** of XV was much slower when Pt black in AcOH was used. Compn. of the alcs. from XV could also. . .

L7 ANSWER 9 OF 22 CAPLUS COPYRIGHT 2002 ACS
TI The **hydrogenation** of acetylene to ethylene
AB The process of selective **hydrogenation** of C2H2 (I) in the presence of Pd has been investigated and it was established that **PdCaCO3**, with additions of Pb, is an active **catalyst** which possesses good selective properties. For a 1:2 mixt. of I and H the max. yield of C2H4 (II) is. . . of I introduced, and up to 100% when calcd. on the amt. of I taking part in the reaction. The **catalyst** preserves its activity for a rather long time, in particular with initial mixts., in which the vol. I is relatively smaller than the vol. H. The deactivated **catalyst** easily recovers its activity when air is blown on it. Addn. of an inert gas to the initial mixt. increases the time of service of the **catalyst** but lowers somewhat the yield of II. Under the same conditions the **hydrogenation** of I is relatively more complete in the vapor phase than in the liquid phase, owing, apparently, to a better contact of I and H with the **catalyst**.

L7 ANSWER 10 OF 22 CAPLUS COPYRIGHT 2002 ACS
AB 11,14-Steroid peroxides are selectively reduced to compds. having OH groups in the nucleus at the same positions by **hydrogenation** in the presence of a Raney nickel **catalyst** or of a poisoned or deactivated palladium **catalyst**. The process is especially useful when a nuclear double bond is present in the 6,7-position as well as in the 8,9-position, since the reduction leaves the 8,9-double bond unchanged. **PdCaCO3** carrier is deactivated with Pb (5% Pd-4% Pb) and satd. with H. A soln. of 0.472 g. isodehydroergosteryl acetate peroxide (I), m. 157.0-8.0.degree., in 30 ml. EtOAc is hydrogenated over 0.2 g. of this **catalyst** at room temp. under 1 atm. H. H absorption ceases abruptly at the end of 2 hrs. after 25.2 ml.. . .

L7 ANSWER 11 OF 22 CAPLUS COPYRIGHT 2002 ACS
AB cf. C.A. 50, 7835i. 3.beta.-Acetoxy-16-cyano-16-androstene (I) and MeMgBr gave 3.beta.-hydroxy-16-acetyl-16-androstene (II) **hydrogenation** of which yielded thermodynamically unstable 3.beta.-hydroxy-16.beta.-acetylandrostane (III) which easily underwent a change to the stable 3.beta.-hydroxy-16.alpha.-acetylandrostane (IV). Configurations of III. . . mg. XVIII 8 hrs. in 10 ml. EtOH over 500 mg. 5% Pd-CaCO3, adding 2

addnl. 200-mg. portions of the **catalyst**, dilg. the mixt. with Et2O, removing the **catalyst**, and evapg. the filtrate gave 48 mg. XX, [.alpha.]D20 6.2.degree.. Hydrogenating 100 mg. VII in 5 ml. dioxane over 50 mg. 5% **PdCaCO3** gave 83 mg. VIII, m. 175-7.degree. (from C6H6), [.alpha.]D20 -9.2.degree.. Keeping the 140 mg. III 20 hrs. at room temp.. . .

=> d l7 kwic 12-18

L7 ANSWER 12 OF 22 CAPLUS COPYRIGHT 2002 ACS
TI Tertiary triatomic alcohols of the acetylenic series and their transformations. VII. **Hydrogenation** of 2,3,6-trimethyl-4-heptyne-2,3,6-triol, 3,4,7-trimethyl-5-octyne-3,4,7-triol, 2-methyl-5-(1-hydroxycyclohexyl)-3-hexyne-2,5-diol, and 2,4-bis(1-hydroxycyclohexyl)-3-butyn-2-ol
AB cf. C.A. 50, 3253g. Pt and Pd **catalysts** cause the **hydrogenation** of acetylenic tertiary glycerols to the corresponding ethylenic alcs., yielding apparently the cis isomers. The **hydrogenation** curves over Pt or Pd have similar character in this group of compds., although the reaction rate over Pt is somewhat greater. Neither **PdCaCO3** nor PtO2 is capable of effecting **hydrogenation** of these compounds to the satd. analogs. In AcOH the Pt **catalyst** causes further absorption of H by the ethylenic derivs. but the reaction takes place at the expense of replacement of. . .

L7 ANSWER 13 OF 22 CAPLUS COPYRIGHT 2002 ACS
AB . . . yielded 60 mg. 3.beta.,17.alpha.-diacetoxy-16-oxoandrostane, m. 152.degree., [.alpha.]D20 -197.degree.. Similar treatment of 3.beta.,16.beta.-diacetoxy-17.alpha.-hydroxyandrostane yielded 82% 3.beta.,16.beta.-diacetoxy-17-oxoandrostane (VIII), m. 156-7.degree., [.alpha.]D20 60.degree.. **Hydrogenation** of VIII over Pt in AcOH gave 62% 3.beta.,16.beta.-diacetoxy-17.beta.-hydroxyandrostane (IX), m. 160-2.degree., [.alpha.]D20 0.degree., the acetylation of which yielded 3.beta.,16.beta.,17.beta.-triacetoxyandrostane,. . . yielded 450 mg. I, m. 147-8.degree., [.alpha.]D20 32.degree.. Treatment of 150 mg. X in 10 ml. EtOH with 300 mg. **PdCaCO3** and H, and after 8 hrs. treating twice with 200-mg. portions of the **catalyst** and H, dilg. the mixt. with Et2O, acidifying with dil. HCl, removing the **catalyst**, washing the ether ext. with NaHCO3 and H2O, evapg. the solvent, and crystg. the residue from MeOH yielded 60 mg.. . .

L7 ANSWER 14 OF 22 CAPLUS COPYRIGHT 2002 ACS
AB . . . yielded 60 mg. 3.beta.,17.alpha.-diacetoxy-16-oxoandrostane, m. 152.degree., [.alpha.]D20 -197.degree.. Similar treatment of 3.beta.,16.beta.-diacetoxy-17.alpha.-hydroxyandrostane yielded 82% 3.beta.,16.beta.-diacetoxy-17-oxoandrostane (VIII), m. 156-7.degree., [.alpha.]D20 60.degree.. **Hydrogenation** of VIII over Pt in AcOH gave 62% 3.beta.,16.beta.-diacetoxy-17.beta.-hydroxyandrostane (IX), m. 160-2.degree., [.alpha.]D20 0.degree., the acetylation of which yielded 3.beta.,16.beta.,17.beta.-triacetoxyandrostane,. . . yielded 450 mg. I, m. 147-8.degree., [.alpha.]D20 32.degree.. Treatment of 150 mg. X in 10 ml. EtOH with 300 mg. **PdCaCO3** and H, and after 8 hrs. treating twice with 200-mg. portions of the **catalyst** and H, dilg. the mixt. with Et2O, acidifying with dil. HCl, removing the **catalyst**, washing the ether ext. with NaHCO3 and H2O, evapg. the solvent, and

crystg. the residue from MeOH yielded 60 mg.. . .

L7 ANSWER 15 OF 22 CAPLUS COPYRIGHT 2002 ACS
AB . . . give 65% [PhCH:CHC(OH)PhCH2C.tplbond.CC(OH)PhCH2CH:]2 (II), C54H4804 II, white crystals, m. 139.degree. (cor.) after sintering at 135.degree. (micro m.p.) (from Me2CO-H2O). Partial **hydrogenation** of the acetylene bonds of II was not successful. Short heating of II with anhyd. toluenesulfonic acid in toluene at. . . in C6H6 525 m.mu., more sol. than III, and orange crystals (V), m. 159.3-9.7.degree., 1st max. in C6H6 522 m.mu.. **Hydrogenation** of III, IV, and V with 5% **PdCaCO3 catalyst** poisoned with Pb according to Lindlar gives mixts. of stereoisomeric 1,3,7,12,18-hexaphenyloctadecanonaenes (VI), which were partially sepd. by chromatography. A no.. . .

L7 ANSWER 16 OF 22 CAPLUS COPYRIGHT 2002 ACS
AB The **hydrogenation** of 11.alpha.-hydroxyprogesterone (I) has been shown to yield mainly pregnan-11.alpha.-ol-3,20-dione (II), which was oxidized to pregnane 3,11,20-trione (III). The differential. . . g. KOH in 3 cc. MeOH hydrogenated at 580 mm. and room temp. 3 hrs. over 0.1 g. 10% Pd-C **catalyst**, the mixt. filtered, the filtrate neutralized with AcOH, concd. in vacuo, dild. with H2O, extd. with Et2O, the ext. evapd.,. . . room temp. gave 0.21 g. III, m. 145-9.degree. (from Me2CO-hexane), analytical sample, m. 158-60.degree., [.alpha.]20D 128.degree., .lambda.CHCl3max. 1702 cm.-1 The **hydrogenation** of I carried out in EtOH under otherwise identical conditions was complete in 15-30 min., yielding 18-20% IX, m. 186-93.degree.;. . . 140-4.degree., while in another run the oxidation of the total mother liquors with CrO3 yielded 40% III, m. 146-50.degree.. The **hydrogenation** of 0.6 g. I with 0.1 cc. piperidine instead of KOH yielded 27% IX, m. 188-95.degree.; acetylation of the mother. . . MeOH hydrogenated 24 hrs. at 30 lb./sq. in. and room temp. over 50 g. prereduced Pd-C, the mixt. filtered, the **catalyst** washed well with hot dioxane, and the combined dioxane soln. poured into 40 l. ice water gave 485 g. (96%. . . EtOH (distd. from Raney Ni), hydrogenated 24 hrs. at 30 lb. pressure and room temp. over 1.5 kg. prereduced 1.5% **PdCaCO3**, the **catalyst** filtered off, washed with hot EtOH, the combined soln. evapd. to a small vol., poured into ice water, and the. . .

L7 ANSWER 17 OF 22 CAPLUS COPYRIGHT 2002 ACS
AB . . . green Carr-Price reaction, .lambda.max. 368 m.mu. (.epsilon. = 46800), which when hydrogenated with PtO2 in AcOH added 10 H2. On **PdCaCO3**-quinoline **catalyst hydrogenation**, VII added 1 mole H2, giving the corresponding C32-diene, C32H44, deep yellow, m. 152-3.degree. (from petr. ether-alc.), .lambda.max. 398 m.mu.. . .

L7 ANSWER 18 OF 22 CAPLUS COPYRIGHT 2002 ACS
AB . . . are produced by condensation of .beta.-ionone with ethers of 1-hydroxy-3-methyl-6-halo-2-hexen-4-yne by the action of Zn, Mg, or Cd, followed by **hydrogenation** and dehydration of the resulting ethers of the condensation products; dehydration is done by acylation, followed by thermal cleavage of. . . b10 71-4.degree., n19D 1.4540; 1-PhO analog, b0.05 75-8.degree., n22D 1.518. The 1-MeO analog and aq. CH2O heated with a Cu **catalyst** to 120.degree. give 70% 1-methoxy-3-methyl-6-hydroxy-2-hexen-4-yne, b15 127-9.degree., n22D 1.496. The OH derivs. with PX3 in the presence of a little. . . with ice and dil. H2SO4, extd. with Et2O, and treated with semicarbazide in MeOH, gave

3-3.5 parts 1-methoxy-3,7-dimethyl-7-hydroxy-9-trimethylcyclohexenyl-2,8-nonadien-4-yne, n20D 1.515; **hydrogenation** over **PdCaCO3** in MeOH gave the 2,4,8-nonatriene, n20D 1.512, without absorption above 260 m.mu. and promoting growth in rats deficient in vitamin. . . with (CO2H)2 gives a similar result. If the dienyne is refluxed 1 hr. with Zn in 80% AcOH the partial **hydrogenation** of the triple bond and dehydration take place in 1 step and the product may be purified as above.

Cf.. . .

=> d l7 kwic 19-22

L7 ANSWER 19 OF 22 CAPLUS COPYRIGHT 2002 ACS

AB By suspending 20 g. Ni(CN)2 **catalyst** (the prepn. of which from NiCl2 is described in detail), 50 g. CaC2, or the equiv. amt. of CH2.O.CH2 in. . . (C.A. 6, 748; 7, 1507). Details are also given of the ultraviolet and infrared absorption and Raman spectra of I. **Hydrogenation** of 10.4 g. I with Pd-C at 22.degree. and 760 mm., or with a Cr-Ni **catalyst** at 80-100.degree. and 100 atm., yielded 9 g. cyclooctane (II), b50 62-3.degree., b760 143.degree., m. 9-10.5.degree.. **Hydrogenation** of 30 g. I in 75 ml. MeOH (or dioxane, Pr2O, EtOH, cyclohexane, etc.) with Pd(1%)-CaCO3 at 30.degree. yielded 26.4 g. odoriferous cyclooctene (III), C8H14, b12 34.degree., nD20 1.4704, d420 0.8500, giving II on **hydrogenation** with Pd-C. Oxidation of III with KMnO4 in Me2CO at 0-10.degree. or H2O at 25-30.degree. with 65% HNO3 or with. . . formation of 23 g. cyclooctenyl deriv. of II (probably 1-cyclooctenyl), b2 135-40.degree., yielding the cyclooctyl deriv., b1 135-40.degree., on Pd-C **hydrogenation** (as indicated by analysis and H sorption). From 110 g. III, 30 g. Ni carbonyl, 25 g. H2O, and CO. . . II, b15 100-1.degree., d420 0.9740, nD20 1.4871 [phenylurethan, m. 60.degree. (from ligroin)], yielding suberic acid on HNO3 oxidation. When the **hydrogenation** of IV was carried out 260 min. at 25-30.degree., 3 moles H were absorbed, yielding C8H8O (?), b18 104-5.degree., nD20. . . and Na. VI with MeOH yielded the cyclooctatriene, b760 145-6.degree., forming a dienemaleic anhydride adduct, C12H12O3, m. 144-5.degree., and on **hydrogenation** yielding II. I (208 g.) added to 600 g. HgSO4 suspended in H2O, formed a colorless Hg addn. product, which. . . and MeOH, 78% PhCH2CH(OMe)2, b22 110.degree.. Oxidation with air in the gaseous phase at 370.degree. in the presence of a **catalyst** contg. 13.7% MoO3, 4.9% V2O5, 6.4% TiO2, and 75% pumice yielded 70% BzOH (and traces of BzH). CrO3 oxidation of. . . MeOHNH3 was used in the sapon. of X.) X (or its ether) gives BzOH with KMnO4 and AcPh with CrO3. **Hydrogenation** of X with Pd-CaCO3 in MeOH or with PtO2 in AcOH never satisfied more than 1/2 of its double bonds.. . . -20 to -30.degree., and with Cl in CCl4. On standing, heating, or distn. XI is in part converted into XII. **Hydrogenation** of a mixt. of 70 g. XII, 50 g. KOH, 40 cc. H2O, 20 g. Raney Ni, and 1 l.. . . g. of a colorless, odorous satd. hydrocarbon, C16H24, b1.5 132-3.degree., nD20 1.5318, d420 1.0231. Shaken and hydrogenated with 20 g. **PdCaCO3** in (iso-Pr)2O, 35 g. XI gave after 0.45 hr. 7,8-dichlorobicyclo[4.2.0]-2(or 3)-octene (XIII), C8H10Cl2, b13 104.degree., nD20 1.5242, converted on further **hydrogenation** into 7, 8-dichlorobicyclo[4.2.0]octane (XIV), b15 110.degree., nD20 1.5069, d420 1.1887, and, on bromination in CH2Cl2, into the 2, 3(or 3,4)-di-Br deriv., C8H10Cl2Br2, prisms, m. 124-5.degree.. The direct **hydrogenation** of XI to XIII could

also be carried out in MeOH at -5.degree., and in tetrahydrofuran with Raney Ni at. . . 122 g. of a mixt. contg. largely 2,3,7,8- or 2,5,7,8-tetrachlorobicyclo[4.2.0]-4(or 3)-octene (XVI), m. 111-12.degree., and a mixt. of isomers C8H8Cl4. **Hydrogenation** of XVI in tetrahydrofuran and KOH (Pd-CaCO3 **catalyst**) gave XIV. Bromination of XV in CHCl3 at 20.degree. yielded the corresponding 4,5- or 3,4-di-Br deriv., C8H8Cl4Br2, m. 101-2.degree. (from. . . was formed the 7, 8-di-AcO analog of XI, m. 66.degree. (from ligroin), and a dimer, C24H28O8, m. 140.degree. (from MeOH). **Hydrogenation** of the monomer gave the 7,8-di-AcO deriv. of XV, fragrant oil, b0.4 105.degree., nD20 1.4662, d420 1.1025, sapon. no. 501;. . . gave 30 g. of a Cl-contg. material (incompletely analyzed), b14 118-20.degree., consisting largely of impure styryl acetate (inasmuch as on **hydrogenation** 1 mole H was added to form AcOCH2CH2Ph, b1 80.degree., d420 1.0765, identified after sapon. as the PhCH2CH2OH urethan, m.. . . impure (halogen-contg.) oily pleasant-smelling di-Me ether, CH:CH.CH2.CH:CH.CH.CH(OMe).COMe (XVII), b8 80.degree., nD20 1.0588, d420 1.0206, which gave anomalous results on catalytic **hydrogenation** with Pd-CaCO3, due possibly to the Cl-contg. impurity and which obviously was not the di-MeO analog of XI. A more satisfactory **hydrogenation** of XVII was effected with Raney Ni in alkali under 100 atm., giving nearly quantitatively 1-methoxy-1-(methoxymethyl)cycloheptane (XVIIa), C10H20O, b9 77.degree.,. . . an oxide of XI, O.CH.CH.CH:CH.CH.CH.CHCl.CHCl, m. 74-5.degree. (from Et2O), together with a liquid isomer, oil, b0.2 96-100.degree., nD20 1.5393. On **hydrogenation** with Pd-CaCO3 in (iso-Pr)2O, the solid oxide took up 2 moles H, forming the compd. C8H12OCl2, CH2.CH2.CH(OH).CH2.CH.CH.CHCl.CHC
l or CH2.CH2.CH2.CH(OH).CH.CH.CHCl.CHCl, m.. . . C22H20O2 (formed from 2 moles I and 1 mole XXIII), yellow prisms, m. 225.degree. (from BuOH) (analytical data lost). Catalytic **hydrogenation** of XXIV gave a tetrahydro deriv., m. 119-20.degree. (from MeOH). I (104 g.) and 158 g. naphthoquinone in boiling xylene. . . C12H8O3, m. 168-70.degree. (from C6H6), giving the corresponding free acid, C12H10O4, m. 158-60.degree., on treatment with NaOH, and on catalytic **hydrogenation**, a hexahydro anhydride, C12H14O3, m. 154-5.degree. (from cyclohexane). These reactions indicate that in the adduct formation with I, addn. on. . . after acidification the trans form of XXV, m. 218.degree. (from MeOH-H2O); impure trans-di-Me ester, mobile oil, b101 60-180.degree.. On pressure **hydrogenation** (Pd-C) at 120.degree. (100 atm.), XVIIIa in aq. KOH (or more slowly at ordinary pressures) gave the tetrahydro deriv. (XXVI) of cis-XXV, m. 168.degree. (decompn.). The same product was formed by a freshly prepd. Cr-Ni **catalyst** and H acting on XVIIIa in MeOH-NaOH at 70-80.degree. and 100 atm. The anhydride of XXVI b9 196-8.degree., m. 126-8.degree.;. . . m. 60-6.degree., b4 160.degree.; di-Et ester, oil, b4 177-8.degree.; di-Bu ester, b4 210.degree.; mono-Me ester, m. 95.degree.. When the Pd-C **hydrogenation** of XXV at ordinary pressure was interrupted after 1 mole H had been sorbed, the cis-dihydro deriv. (XXVII) of XXV,. . . (from C6H6); di-Me ester of XXVII, b2 158-60.degree., m. 28-31.degree.; di-Et ester, oil, b2 164-6.degree.; di-Bu ester, oil, b2 188-90.degree.. **Hydrogenation** of XXVII gave a tetrahydro acid, m. 151.degree. (decompn.), yielding the anhydride of XXVI, m. 128-9.degree.. The tetrahydro deriv. of. . . aq. MeOH), was formed (a) from the cis isomer by heating its Me ester with

MeONa; or (b) through Pd-C **hydrogenation** of the trans form of XXV. The dihydro deriv. of trans-XXV, C12H14O4, m. 209-11.degree. (from aq. MeOH), was formed by partial **hydrogenation** of trans-XXV, or by the inversion of the Me ester of XXVII. Br (18 g.) in 100 ml. MeOH added. . . isomeric hexachlorobutanes [probably (CHCl2CHCl)2], a cryst. solid, m. 109-10.degree. (from C6H6), and an oil, b10 111.degree., nD20 1.5258, d420 1.6460. **Hydrogenation** of XXX in MeOH with Pd-CaCO3 at room temp. was slow and incomplete. However, with Pd-C in the presence of KOH in MeOH, 3 moles H were taken up within 7 hrs., giving cyclobutane, b. 2-7.5.degree.. When the **hydrogenation** (at room temp.) was extended to 10 hrs., XXX reacted with 4 moles H, yielding butane, b. -0.1 to 1.5.degree... . . another product (3, 4-diacetoxycyclobutene) which was lost. The adduct, C12H10O4, of IV with CO.CH:CH.CO.O, m. 203.degree., was formed in C6H6; **hydrogenation** yielded the dihydro deriv., m. 240-5.degree. (from C6H6). (.tplbond.CCO2Me)2 with IV in C6H6 yielded the adduct, C14H14O5, m. 103.degree. (front. . . a solvent. When the reaction was carried to 120-30.degree., followed by vacuum distn., o-C6H4(CO2Me)2 and resinous products were formed. Catalytic **hydrogenation** of C14H14O5 gave the tetrahydro deriv., m. 86-7.degree. (from Et2O). In C6H6, XI gave an adduct with XXIII, m. about. . . was an isomeric dimer, C6H16, b1 138.degree., m. 44.degree. (by vacuum distn., or cooling an Et2O soln. to -80.degree.). Dimerization **of I** could also be effected by heating in 3 parts o-C6H4Cl2, in which case both dimers were formed, with the solid. . .

L7 ANSWER 20 OF 22 CAPLUS COPYRIGHT 2002 ACS

AB . . . gave p-menthen-4-ol (I), b3 70-1.degree., d204 0.9266, n20C 1.47313, n20D 1.47604, n20F 1.48308, [.alpha.]20D -24.32.degree.. I with 2% Raney Ni **catalyst** at 125-30.degree. and 8 kg./sq. cm. pressure of H gave 4-p-menthanol (II), m. 53.degree. (from pentane) [phenylurethan, m. 140.degree. (from. . . the product from (b) with 96% H2SO4 30 min. failed to give the phys. consts. of the product from (c). **Hydrogenation** of these hydrocarbons with PtO2 **catalyst** at 60.degree. in AcOEt gave from (a) and (b) (cis- and trans-p-menthane) and (c) (dimethylisopropylcyclopentane) products whose consts. are, resp.:. . . 1.43997, 1.43201; n20F 1.44562, 1.44550, 1.43753. Dehydrogenation of the reaction products by distn. of 5 cc./hr. over 20 g. Pd-C **catalyst** in a tube at 300.degree. and repassing once gave evidence of the presence of cis- and trans-p-menthanes by the isolation. . . (28 g.), b733 162-3.degree., d204 0.8437, n20C 1.46749, n20D 1.47082, n20F 1.47891, reduced in dioxane with H and 0.02 g. **PdCaCO3** at 20.degree. gave in 110 min. (90% theoretical uptake in 40 min.) dihydrosabinene (V), b735 156.2-6.4.degree., d204 0.8123, n20C 1.44628,. . .

L7 ANSWER 21 OF 22 CAPLUS COPYRIGHT 2002 ACS

AB . . . with 25% acid. The structures of the isomerization products are indicated by their absorption spectra and rigidly proved by complete **hydrogenation** to known satd. carbinols. Both active H atoms in conjugated ethynylvinylcarbinols, unlike those of their unconjugated isomers, react completely in the cold with MeMgI. CH.tplbond.CNa (prepd. from 36 g. Na in 1 l. liquid NH3, using Fe(NO3)3 **catalyst**) and

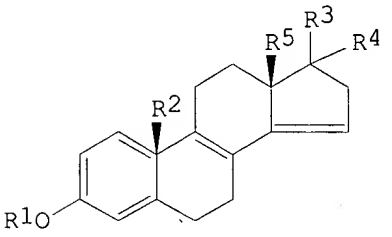
24 g. Me vinyl ketone in 250 cc. dry ether (added during 1.5 hrs. with stirring and cooling (Me2CO-solid. . . hrs., give 15 g. of 2,4-dimethyl-3-hexen-5-yn-2-ol, b20 65-6.degree., nD19 1.4711. II (11 g.)
in 30 cc. AcOMe, reduced with 0.3% **PdCaCO3**, gives 10.7 g. of 3-methyl-1,4-hexadien-3-ol (IV), b15 41.5-2.5.degree., b28 56-8.degree., nD13 1.4485. IV (6 g.) and 400 cc. 0.5% H2SO4,. . .

L7 ANSWER 22 OF 22 CAPLUS COPYRIGHT 2002 ACS
AB . . . CHCl3 (with cooling) give di-Me 3,6-endoxo-1,2,4,5-tetrabromohexahydro-o-phthalate (XA), m. 219-20.degree. (from MeCN); partial dehalogenation of 3 g. XA with 10 g. **PdCaCO3** in 250 cc. dioxane gives a dibromotetrahydro deriv., m. 127-8.degree.; a product (XI)
prepd. from 106 g. VI and 51. . . g. of XV in EtOH with 0.1 g. Pd gives
the hexahydro deriv. (XVA), m. 121.5.degree.; a larger amt. of **catalyst** should not be used, the product then being succinic acid or anhydride. XV (4 g.) in 200 cc. CS2 and. . . tetrolate in a sealed tube at 145.degree. for 7.5 hrs. gives 1,4,5,8-diendomethylene-9-methyl-10-carbethoxy-.DELTA.2,6-hexalin (XIX), a yellow oil, b1.5 above 152.degree.;
definite **hydrogenation** products could not be isolated. Passing a stream of C2H2 into boiling 2,5-dimethylfuran for 10 hrs. and distn. of the. . .

L9 ANSWER 1 OF 4 CAPLUS COPYRIGHT 2003 ACS
AN 1992:129376 CAPLUS
DN 116:129376
TI Selective catalytic **hydrogenation** of steroid 9(9); 14(15)-dienes with aromatic A ring
IN Ring, Sven; Stopsack, Heinz; Scharff, Armin; Lahne, Christine; Siebert, Jochen
PA Jenapharm G.m.b.H., Germany
SO Ger. (East), 3 pp.
CODEN: GEXXA8
DT Patent
LA German
FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DD 294488	A5	19911002	DD 1985-285838	19851231

PRAI DD 1985-285838 19851231
OS CASREACT 116:129376; MARPAT 116:129376
GI



I

AB The 14,15-double bond of steroids I (R1 = H, alkyl, acyl, aryl, silyl, tosyl; R2, R5 = H, alkyl; R3 = OH, alkoxy, acyloxy, siloxy, tosyloxy, R4 = H; R3R4 = O) was reduced selectively over Pd-MgCO3 catalyst. The catalyst shows improved selectivity and is easily sepd. from the support. Thus, I (R1, R5 = Me, R2, R4 = H, R3 = .beta.-OH) was reduced over Pd-MgCO3 to give 96% 3-methoxy-1,3,5(10),8-estratetraen-17.beta.-ol.

L9 ANSWER 2 OF 4 CAPLUS COPYRIGHT 2003 ACS
AN 1975:563353 CAPLUS
DN 83:163353
TI Catalytic properties of **palladium** on **magnesium carbonate** in **hydrogenation** reactions
AU Mambetkazieva, R. A.
CS USSR
SO Katalitich. reaktsii v zhidk. faze. (1974), (Ch. 1), 118-20
From: Ref. Zh., Khim. 1975, Abstr. No. 4B1260
DT Journal
LA Russian
AB Title only translated.

L9 ANSWER 3 OF 4 USPATFULL
AN 2001:179308 USPATFULL
TI Method of hydrogenating iso-.alpha. acids in a buffered solution

IN Ting, Patrick L., Brookfield, WI, United States
Hoppe, Steven M., Watertown, WI, United States
Navarro, Alfonso, Milwaukee, WI, United States
Goldstein, Henry, Brookfield, WI, United States
Ryder, David S., Mequon, WI, United States
PA Miller Brewing Company, Milwaukee, WI, United States (U.S. corporation)
PI US 6303824 B1 20011016
AI US 1999-438721 19991111 (9)
DT Utility
FS GRANTED
EXNAM Primary Examiner: Geist, Gary; Assistant Examiner: Deemie, Robert W.
LREP Quarles & Brady LLP
CLMN Number of Claims: 12
ECL Exemplary Claim: 1
DRWN No Drawings
LN.CNT 363
CAS INDEXING IS AVAILABLE FOR THIS PATENT.
AB A method of preparing tetrahydroiso-.alpha.-acids from iso-.alpha.-acids
is disclosed wherein the reaction medium is a buffered, aqueous alcoholic solution. The method can also employ up to 85% w/w spent **hydrogenation** catalyst. The method advantageously avoids the formation of undesirable side products.

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L9 ANSWER 4 OF 4 USPATFULL
AN 1998:147447 USPATFULL
TI Imidazopyridine or imidazopyrimidine compounds, their production and use
IN Takatani, Muneo, Kyoto, Japan
Ikeda, Hitoshi, Higashiosaka, Japan
Iida, Kyoko, Osaka, Japan
Abe, Hidenori, Osaka, Japan
PA Takeda Chemical Industries Ltd., Osaka, Japan (non-U.S. corporation)
PI US 5840732 19981124
WO 9535296 19951228
AI US 1996-481391 19961206 (8)
WO 1995-JP1192 19950615
19961206 PCT 371 date
19961206 PCT 102(e) date
PRAI JP 1994-137600 19940620
JP 1995-64128 19950323
DT Utility
FS Granted
EXNAM Primary Examiner: Higel, Floyd D.
LREP Foley & Lardner
CLMN Number of Claims: 51
ECL Exemplary Claim: 1
DRWN No Drawings
LN.CNT 6940
CAS INDEXING IS AVAILABLE FOR THIS PATENT.
AB This invention provides a new condensed imidazole compound possessing inhibitory activity of adhesion molecule expression.

This invention also provides a therapeutic and prophylactic agent for diabetic nephritis and/or autoimmune disease and an immunosuppressor for
organ transplantation.

The catalysts which may be regenerated in accordance with the present method are the noble metal **hydrogenation** catalysts, namely: **palladium**; **platinum**; ruthenium; rubidium; rodium and iridium. The catalyst may be either unsupported on a carrier or supported on a carrier of sufficient particle size. The carrier can consist of alumina, silica gel, carbon, **magnesium carbonate**, dolomite and the like. Formation of these catalysts are old and is described in U.S. Pat. No. 3,635,841.

SUMM . . . another form. For example, the transition temperature of a palladium catalyst is about 380.degree.C and the transition temperature of a **platinum** catalyst is about 590.degree.C.

L8 ANSWER 5 OF 6 USPATFULL
AN 75:43596 USPATFULL
TI Process of regenerating a noble metal **hydrogenation** catalyst used in hydrogen peroxide production by the anthraquinone process
IN Browning, Jhonce N., So. Charleston, WV, United States
Lee, Nathan D., Lambertville, NJ, United States
Smee, George H., So. Charleston, WV, United States
PA FMC Corporation, New York, NY, United States (U.S. corporation)
PI US 3901822 19750826
AI US 1973-415631 19731114 (5)
DT Utility
FS Granted
EXNAM Primary Examiner: Douglas, Winston A.; Assistant Examiner: Konopka, P. E.
CLMN Number of Claims: 13
ECL Exemplary Claim: 1,12
DRWN No Drawings
LN.CNT 455
CAS INDEXING IS AVAILABLE FOR THIS PATENT.
AB This invention describes a process for regenerating deactivated noble metal **hydrogenation** catalysts to restore their catalytic activity. The process involves contacting a deactivated noble metal **hydrogenation** catalyst with a polar organic solvent, then contacting the solvent-treated catalyst with an aqueous ammonium hydroxide solution followed by contacting the ammonium hydroxide-treated catalyst with steam and an oxygen-containing gas at temperatures from about 250.degree.C to the transition temperature of the catalyst crystal structure whereby the catalytic activity of the catalyst is substantially improved.

L12 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2003 ACS
AN 1999:813729 CAPLUS
DN 132:39639
TI Perturbed Angular Correlation Characterization of Indium Species on In/H-ZSM5 Catalysts
AU Miro, E. E.; Gutierrez, L.; Ramallo Lopez, J. M.; Requejo, F. G.
CS INCAPE (CONICET), Fac. Ingenieria Quimica, UNL Argentina, Santa Fe, Argent.
SO Journal of Catalysis (1999), 188(2), 375-384
CODEN: JCTLA5; ISSN: 0021-9517
PB Academic Press
DT Journal
LA English
AB Silicalite-supported indium catalysts (In/H-ZSM5) were characterized by time differential perturbed angular correlation (PAC) and temp.-programmed redn. (TPR). The presence of different indium species was correlated with activity and selectivity during the NO selective catalytic redn. (SCR) with CH4 in the presence of excess oxygen. The main species identified on the In/H-ZSM5 surface were In2O3 (indium sesquioxide crystals); In+Z- and (InO)+Z- (different indium species exchanged in the zeolitic matrix); and highly dispersed noncryst. In oxide species not bonded to the zeolitic matrix. Catalysts that were impregnated and then calcined at 500.degree. had low activity for the reaction under study, showing the presence of only In2O3 and noncryst. In oxide species. Treatment at 750.degree. in O2 or at 500.degree. in H2 followed by reoxidn. at the same temp. resulted in active catalysts showing an appreciable concn. of (InO)+Z- active species. The same active species were formed after indium ion exchange of **NH4-ZSM5** was followed by calcination at 500.degree.. The PAC technique proved to be a powerful tool for the identification and quantification of indium species present on the surface of an H-ZSM5 support. (c) 1999 Academic Press.
RE.CNT 30 THERE ARE 30 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

=> d l12 kwic

L12 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2003 ACS
AB . . . catalysts showing an appreciable concn. of (InO)+Z- active species. The same active species were formed after indium ion exchange of **NH4-ZSM5** was followed by calcination at 500.degree.. The PAC technique proved to be a powerful tool for the identification and quantification. . .

=> d his

(FILE 'HOME' ENTERED AT 11:45:29 ON 03 JAN 2003)

FILE 'CAPLUS, USPATFULL' ENTERED AT 11:46:10 ON 03 JAN 2003
L1 25194 S MAGNESIUM CARBONATE
L2 2282 S L1 AND PALLADIUM

```
L3          1126 S L2 AND PLATINUM
L4             0 S L3 AND PTMGCO3
L5             0 S L3 AND PDMGCO3
L6            48 S PALLADIUM (S) MAGNESIUM CARBONATE
L7            10 S L6 AND HYDROGENATION
L8             6 S L7 AND PLATINUM
L9             4 S L7 NOT L8

     FILE 'REGISTRY' ENTERED AT 11:58:11 ON 03 JAN 2003
L10            1 S 7440-05-3/RN

     FILE 'CAPLUS, USPATFULL' ENTERED AT 11:58:55 ON 03 JAN 2003
L11            0 S ZM5-NH4
L12            1 S NH4-ZSM5
```

(FILE 'HOME' ENTERED AT 11:45:29 ON 03 JAN 2003)

FILE 'CAPLUS, USPATFULL' ENTERED AT 11:46:10 ON 03 JAN 2003

L1	25194	S	MAGNESIUM CARBONATE
L2	2282	S	L1 AND PALLADIUM
L3	1126	S	L2 AND PLATINUM
L4	0	S	L3 AND PTMGCO3
L5	0	S	L3 AND PDMGCO3
L6	48	S	PALLADIUM (S) MAGNESIUM CARBONATE
L7	10	S	L6 AND HYDROGENATION
L8	6	S	L7 AND PLATINUM
L9	4	S	L7 NOT L8

FILE 'REGISTRY' ENTERED AT 11:58:11 ON 03 JAN 2003

L10	1	S	7440-05-3/RN

FILE 'CAPLUS, USPATFULL' ENTERED AT 11:58:55 ON 03 JAN 2003

L11	0	S	ZM5-NH4
L12	1	S	NH4-ZSM5
L13	19451	S	ZSM?
L14	109	S	ZSM5 (P) AMMONI?
L15	54	S	L14 AND AMMONIUM
L16	12	S	L15 AND PALLADIUM
L17	0	S	L16 AND PDNH4-ZSM5
L18	12	S	L16 AND HYDROGEN?

L1 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2002 ACS
AN 1951:5985 CAPLUS
DN 45:5985
OREF 45:1008f-i,1009a-d
TI Stereochemical studies of olefinic compounds. II. Ring scission of 2-(1-haloalkyl)tetrahydrofurans and 3-halo-2-alkyltetrahydropyrans as a route to 4-alken-1-ols of known configuration and as a method of chain extension by five methylene groups
AU Crombie, Leslie; Harper, Stanley H.
CS King's Coll., London
SO J. Chem. Soc. (1950) 1707-14
DT Journal
LA Unavailable
AB cf. C.A. 44, 7753d. Furfural (240 g.), added (4 hrs.) to MeMgI (444 g. MeI and 80 g. Mg) in 900 ml. ether, gives 65% 2-(1-hydroxyethyl)furan (I), b21 80.5.degree., n20D 1.4794; catalytic reduction (3 hrs.) of 70.5 g. I in 200 ml. EtOH over 7 g. Raney Ni at 100.degree./125 atm. gives 89% 2-(1-hydroxyethyl)tetrahydrofuran (II), b20 75-7.degree., n20D 1.4480, mushroom odor. II, SOCl2, and C5H5N, even at -20.degree., give mainly a resin and only a trace of the chloride; HCl behaves similarly. II (5.8 g.) and 0.55 g. red P, treated gradually with 6.35 g. iodine (with final heating at 100.degree.), gives a a crude iodide, yielding 2 fractions b3 45-8.degree., n22D 1.4845 (1.7 g.), and b3 100-3.degree., n22D 1.5540 (1.2 g.). II (27 g.) and 3 ml. C5H5N, added dropwise to 22.4 g. PBr3 and 1 ml. C5H5N at 0.degree. and kept 48 hrs. at room temp., give 34% crude bromide (III), b14 68-100.degree., n23D 1.4740-4. III (10 g.) in 25 ml. ether, added dropwise to 3.5 g. powd. Na in 25 ml. ether, gives 54% MeCH:CH(CH2)3OH [mainly trans-isomer (IV); some cis-isomer (V) present]. This method is unsatisfactory because of the mediocre yields and the apparent impurity of the product. Dihydropyran (168 g.) in 400 ml. ether at 0-5.degree., treated about 2.5 hrs. with Cl, the ether soln. added to 1.5 mols. MeMgBr in an ice bath, kept overnight at room temp., and the product decompd. with NH4Cl and concd. HCl, gives 61% 3-chloro-2-methyltetrahydropyran (VI), fractional distn. of which gives the trans-isomer (VII), b18 51.degree., b. 154.degree., d214 1.071, n21D 1.4551, and the cis-isomer (VIII), b18 66.degree., b. 172.degree., d214 1.091, n21D 1.4626. When 1 mol. MeMgI is added to 2,3-dichlorotetrahydropyran (IX), resinification occurs and scarcely any VI is formed. Powd. Na (144 g.) in 1 l. ether, treated dropwise with 380 g. VI (gentle refluxing), stirred an addnl. 2 hrs., and kept overnight, gives 82% IV; VII similarly gives 87% .alpha.-MeCH:CH(CH2)3OH (X), b. 158.degree., n20D 1.4403, and VIII gives 78% of the .beta.-isomer (XI), b. 159.degree., n20D 1.4402; VIII reacts more vigorously with Na than does VII. Neither the 1-naphthylurethan nor the 4-biphenylylurethan of X or XI depressed the m.p. of the corresponding deriv. of IV. IV (61.5 g.) in an equal vol. of ether, treated (2-3 hrs.) with 99 g. Br at a temp. below 10.degree. and the 4,5-di-Br deriv. added to NaNH2 (70 g. Na in 2 l. liquid NH3), stirred 3 hrs., treated with 100 ml. ether, the NH3 allowed to evap. overnight, and the product extd. with ether, gives 31% 4-hexen-1-ol (XII), b. 165-8.degree., n20D 1.4586 (1-naphthylurethan, m. 82.degree.). XII (5 g.), added dropwise to 5 g. Na in 250 ml. liquid NH3 (cooled in EtOH-solid CO2), and stirred 90 min., gives 72% IV, b. 158.degree., n20D 1.4402 (1-naphthylurethan, m. 72.degree.;

4-biphenylylurethan, m. 93.degree.). Reduction of XII with **PtCaCO3** gives 75% V, b. 158-9.degree., n20D 1.4420 (1-naphthylurethan, m. 74-5.degree.; 4-biphenylylurethan, m. 77.5.degree.). X and XI are identical with IV; the trans configuration is supported by infrared absorption spectra; the spectra of IV, X, and XI are closely similar and differ markedly from that of V; the spectra of X and XI give no indication of the presence of V. IX and 0.9, 1.1, 1.3, and 1.5 mols. EtMgBr give, resp., 42, 52, 53, and 61% 3-chloro-2-ethyltetrahydropyran (contg. both cis and trans isomers); ring scission gives trans-EtCH:CH(CH2)3OH, b11 74-6.degree., n20D 1.4439. IX and PrMgBr give 62% of cis- and trans-3-chloro-2-propyltetrahydropyrans, b18 85-7.degree., n20D 1.4588; ring scission gives 88% trans-4-octen-1-ol, b11 86-8.degree., n20D 1.4456. IX and BuMgBr give 63% of the two 3-chloro-2-butyltetrahydropyrans, b11 83-90.degree., n20D 1.4532, and b11 103-8.degree., n20D 1.4670; the mixt. yields 84% trans-4-nonen-1-ol, b13 101-5.degree., n20D 1.4476. The last 3 compds. are assigned the trans configuration from the infrared spectra. The ring scission of 3-chloro-2-alkyltetrahydropyrans is believed to provide a general route to trans-4-alken-1-ols.

L13 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2002 ACS
AN 1951:5985 CAPLUS
DN 45:5985
OREF 45:1008f-i,1009a-d
TI Stereochemical studies of olefinic compounds. II. Ring scission of 2-(1-haloalkyl)tetrahydrofurans and 3-halo-2-alkyltetrahydropyrans as a route to 4-alken-1-ols of known configuration and as a method of chain extension by five methylene groups
AU Crombie, Leslie; Harper, Stanley H.
CS King's Coll., London
SO J. Chem. Soc. (1950) 1707-14
DT Journal
LA Unavailable
AB cf. C.A. 44, 7753d. Furfural (240 g.), added (4 hrs.) to MeMgI (444 g. MeI and 80 g. Mg) in 900 ml. ether, gives 65% 2-(1-hydroxyethyl)furan (I), b21 80.5.degree., n20D 1.4794; catalytic reduction (3 hrs.) of 70.5 g. I in 200 ml. EtOH over 7 g. Raney Ni at 100.degree./125 atm. gives 89% 2-(1-hydroxyethyl)tetrahydrofuran (II), b20 75-7.degree., n20D 1.4480, mushroom odor. II, SOCl2, and C5H5N, even at -20.degree., give mainly a resin and only a trace of the chloride; HCl behaves similarly. II (5.8 g.) and 0.55 g. red P, treated gradually with 6.35 g. iodine (with final heating at 100.degree.), gives a a crude iodide, yielding 2 fractions b3 45-8.degree., n22D 1.4845 (1.7 g.), and b3 100-3.degree., n22D 1.5540 (1.2 g.). II (27 g.) and 3 ml. C5H5N, added dropwise to 22.4 g. PBr3 and 1 ml. C5H5N at 0.degree. and kept 48 hrs. at room temp., give 34% crude bromide (III), b14 68-100.degree., n23D 1.4740-4. III (10 g.) in 25 ml. ether, added dropwise to 3.5 g. powd. Na in 25 ml. ether, gives 54% MeCH:CH(CH2)3OH [mainly trans-isomer (IV); some cis-isomer (V) present]. This method is unsatisfactory because of the mediocre yields and the apparent impurity of the product. Dihydropyran (168 g.) in 400 ml. ether at 0-5.degree., treated about 2.5 hrs. with Cl, the ether soln. added to 1.5 mols. MeMgBr in an ice bath, kept overnight at room temp., and the product decompd. with NH4Cl and concd. HCl, gives 61% 3-chloro-2-methyltetrahydropyran (VI), fractional distn. of which gives the trans-isomer (VII), b18 51.degree., b. 154.degree., d214 1.071, n21D 1.4551, and the cis-isomer (VIII), b18 66.degree., b. 172.degree., d214 1.091, n21D 1.4626. When 1 mol. MeMgI is added to 2,3-dichlorotetrahydropyran (IX), resinification occurs and scarcely any VI is formed. Powd. Na (144 g.) in 1 l. ether, treated dropwise with 380 g. VI (gentle refluxing), stirred an addnl. 2 hrs., and kept overnight, gives 82% IV; VII similarly gives 87% .alpha.-MeCH:CH(CH2)3OH (X), b. 158.degree., n20D 1.4403, and VIII gives 78% of the .beta.-isomer (XI), b. 159.degree., n20D 1.4402; VIII reacts more vigorously with Na than does VII. Neither the 1-naphthylurethan nor the 4-biphenylylurethan of X or XI depressed the m.p. of the corresponding deriv. of IV. IV (61.5 g.) in an equal vol. of ether, treated (2-3 hrs.) with 99 g. Br at a temp. below 10.degree. and the 4,5-di-Br deriv. added to NaNH2 (70 g. Na in 2 l. liquid NH3), stirred 3 hrs., treated with 100 ml. ether, the NH3 allowed to evap. overnight, and the product extd. with ether, gives 31% 4-hexen-1-ol (XII), b. 165-8.degree., n20D 1.4586 (1-naphthylurethan, m. 82.degree.). XII (5 g.), added dropwise to 5 g. Na in 250 ml. liquid NH3 (cooled in EtOH-solid CO2), and stirred 90 min., gives 72% IV, b. 158.degree., n20D 1.4402 (1-naphthylurethan, m. 72.degree.;

4-biphenylylurethan, m. 93.degree.). Reduction of XII with **PtCaCO3** gives 75% V, b. 158-9.degree., n20D 1.4420 (1-naphthylurethan, m. 74-5.degree.; 4-biphenylylurethan, m. 77.5.degree.). X and XI are identical with IV; the trans configuration is supported by infrared absorption spectra; the spectra of IV, X, and XI are closely similar and differ markedly from that of V; the spectra of X and XI give no indication of the presence of V. IX and 0.9, 1.1, 1.3, and 1.5 mols. EtMgBr give, resp., 42, 52, 53, and 61% 3-chloro-2-ethyltetrahydropyran (contg. both cis and trans isomers); ring scission gives trans-EtCH:CH(CH2)3OH, b11 74-6.degree., n20D 1.4439. IX and PrMgBr give 62% of cis- and trans-3-chloro-2-propyltetrahydropyrans, b18 85-7.degree., n20D 1.4588; ring scission gives 88% trans-4-octen-1-ol, b11 86-8.degree., n20D 1.4456. IX and BuMgBr give 63% of the two 3-chloro-2-butyltetrahydropyrans, b11 83-90.degree., n20D 1.4532, and b11 103-8.degree., n20D 1.4670; the mixt. yields 84% trans-4-nonen-1-ol, b13 101-5.degree., n20D 1.4476. The last 3 compds. are assigned the trans configuration from the infrared spectra. The ring scission of 3-chloro-2-alkyltetrahydropyrans is believed to provide a general route to trans-4-alken-1-ols.

=>